SUPPLEMENTARY INFORMATION

Utility of α-halodicyclopentadienones for the synthesis of novel fused heterocycles

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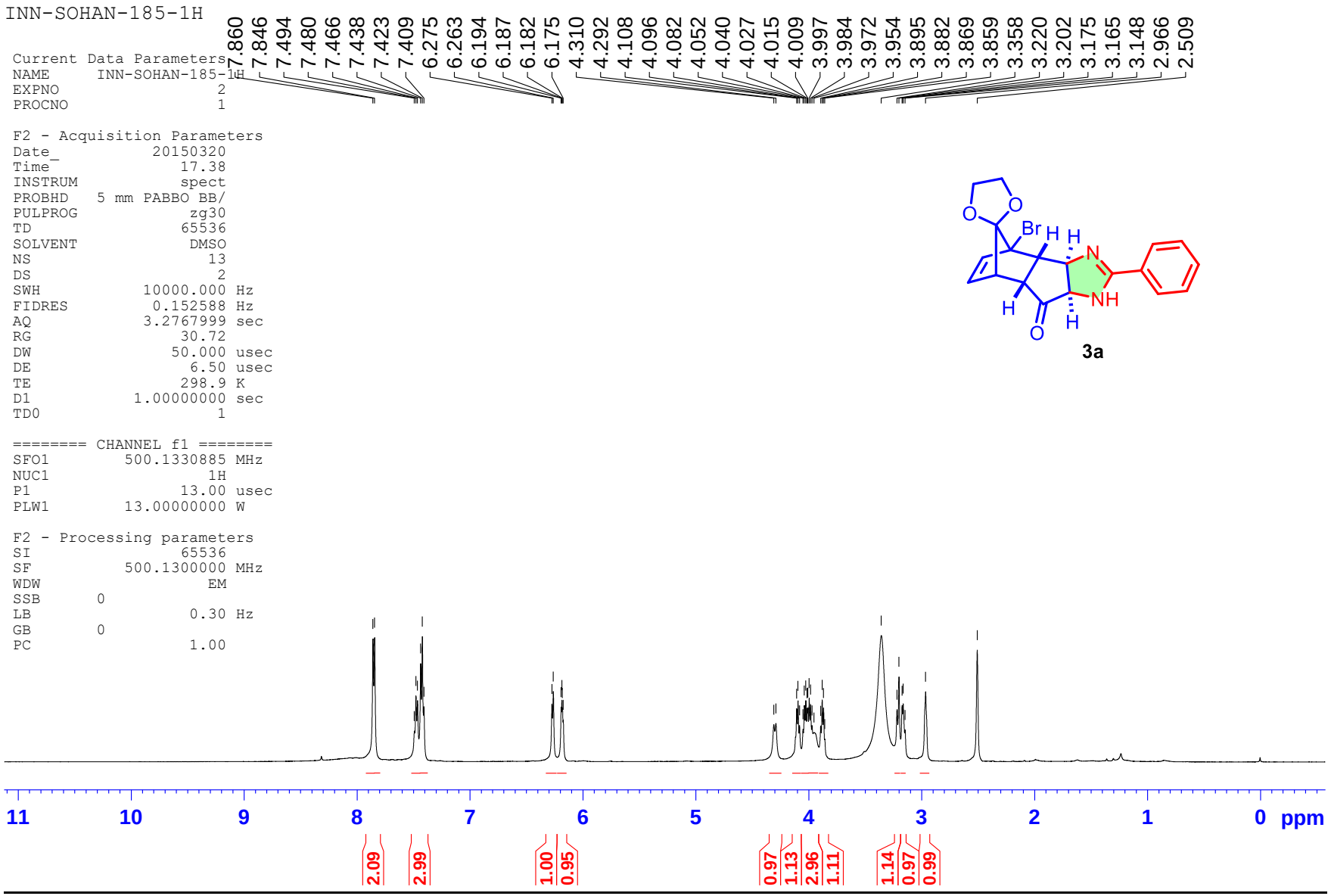


Figure S1. ^{1}H NMR of compound **3a**

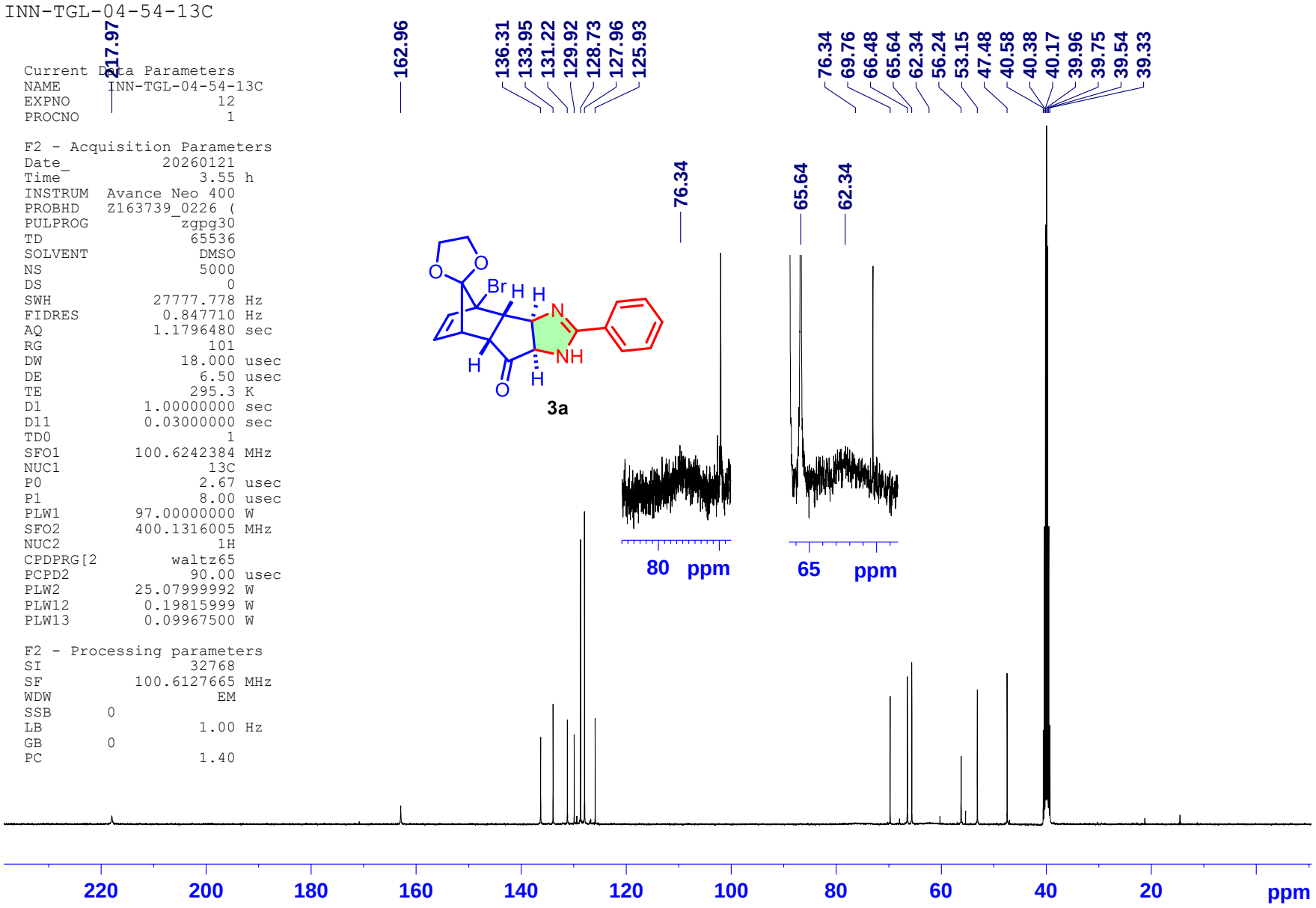


Figure S2. ^{13}C NMR of compound **3a**

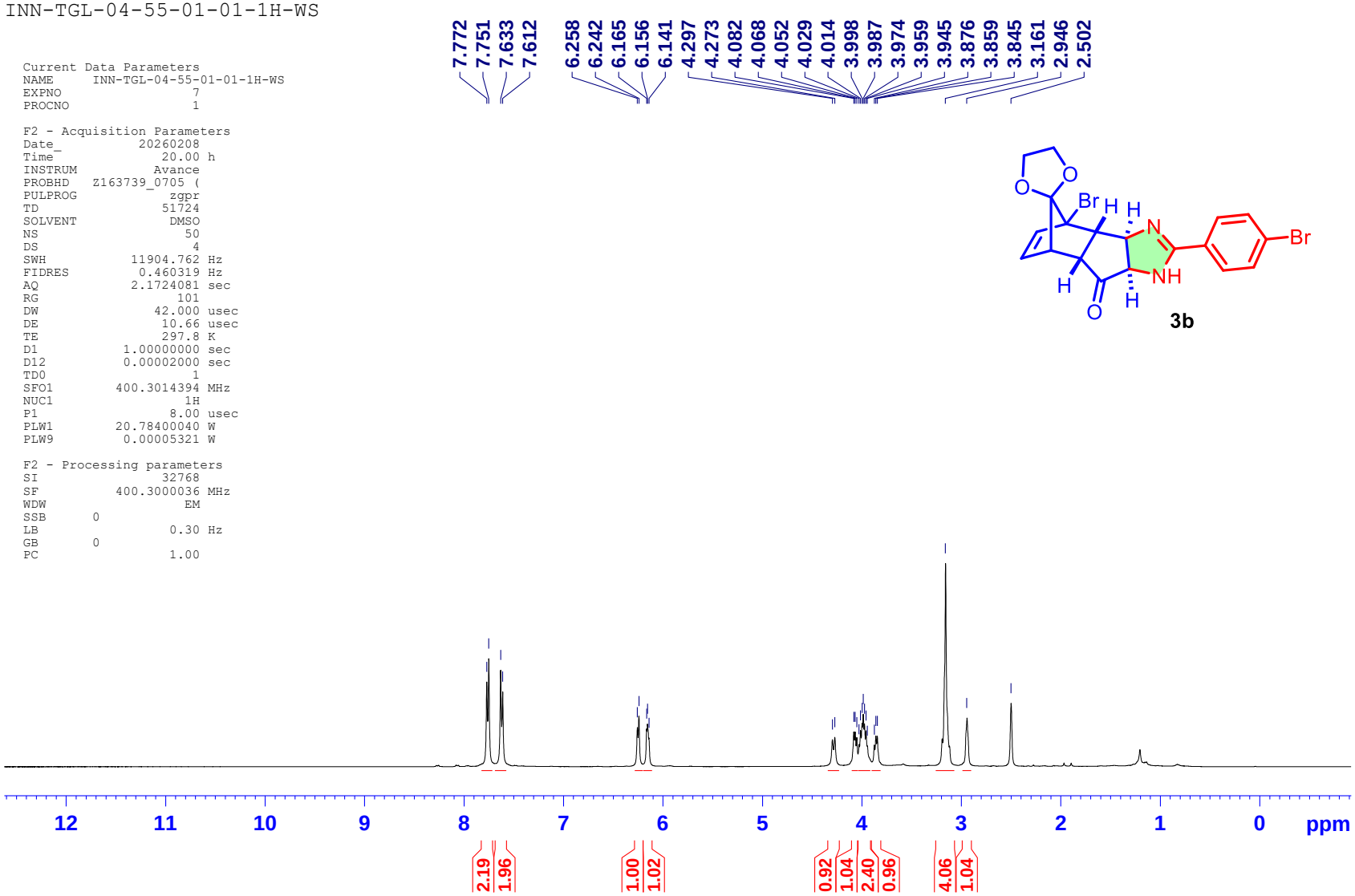
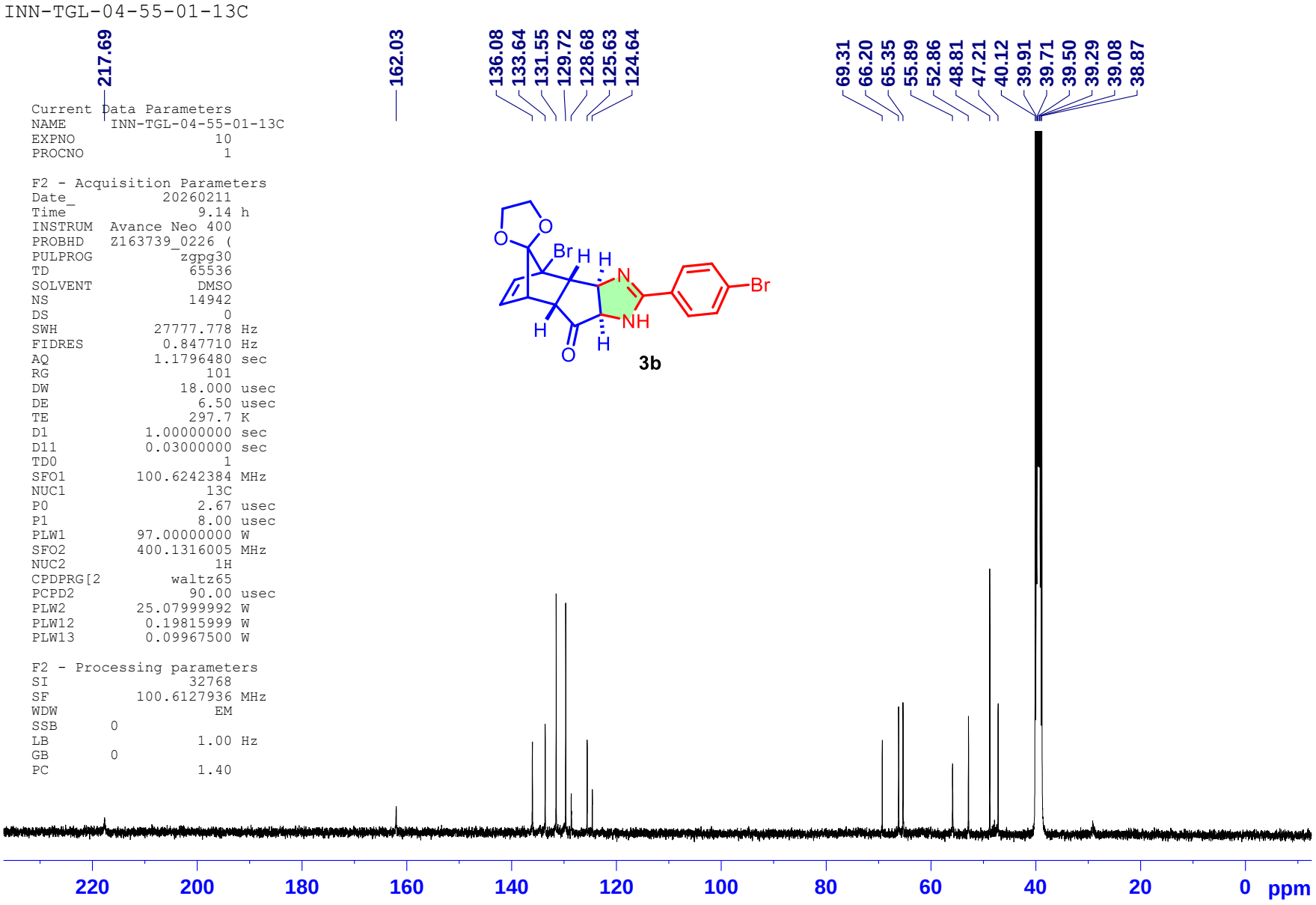


Figure S3. ^{1}H NMR of compound **3b**



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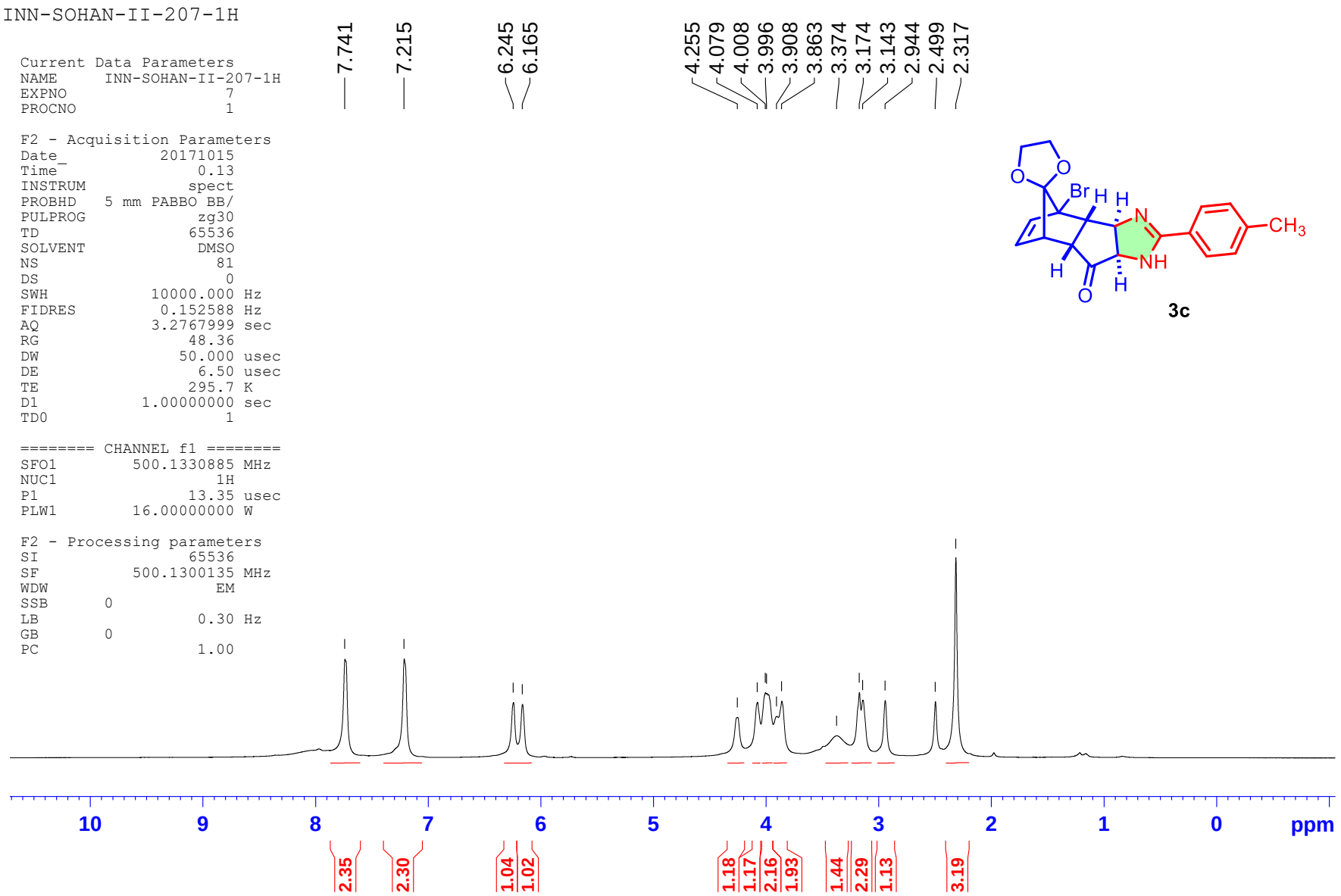


Figure S5. ^{1}H NMR of compound **3c**

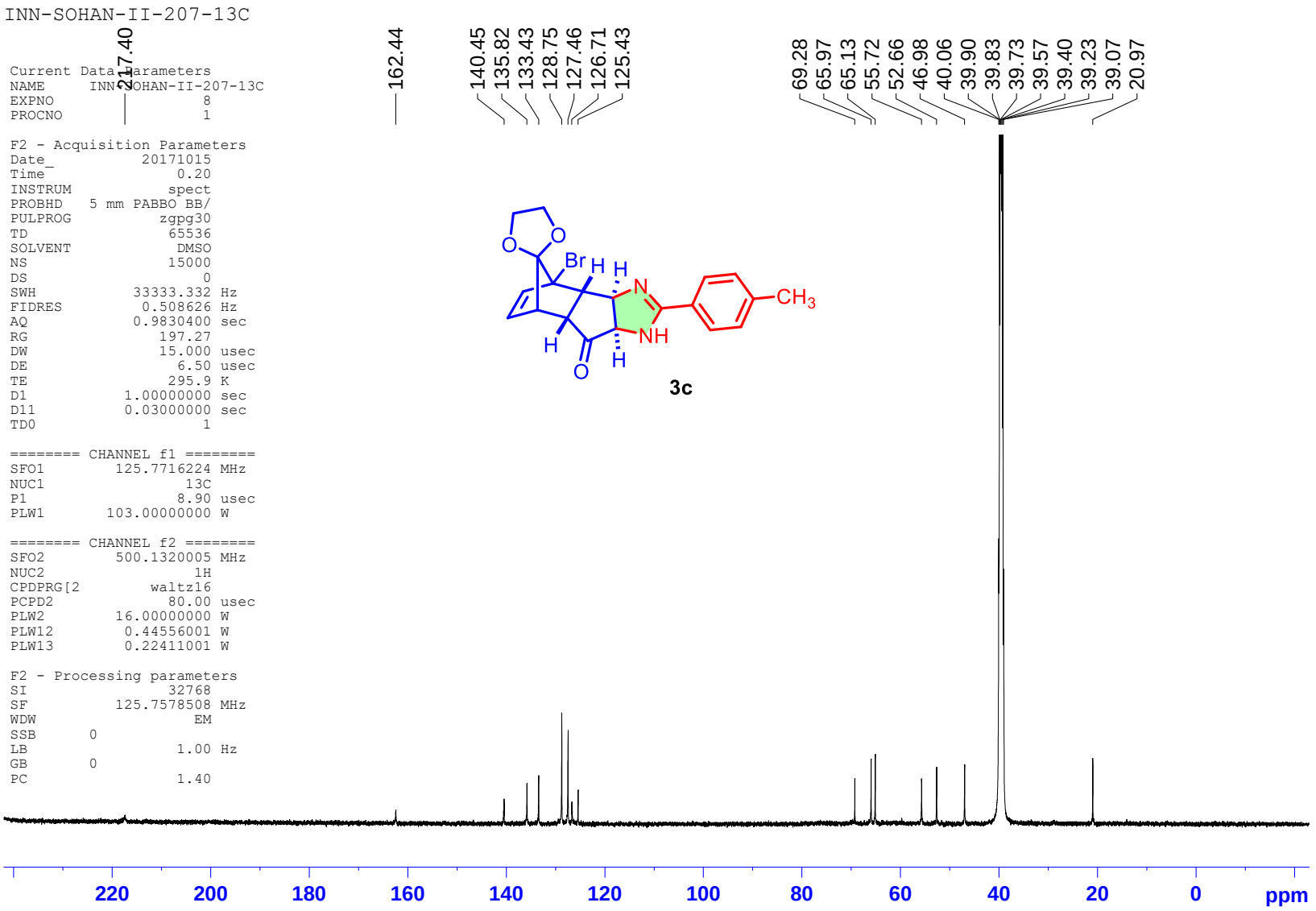


Figure S6. ^{13}C NMR of compound **3c**

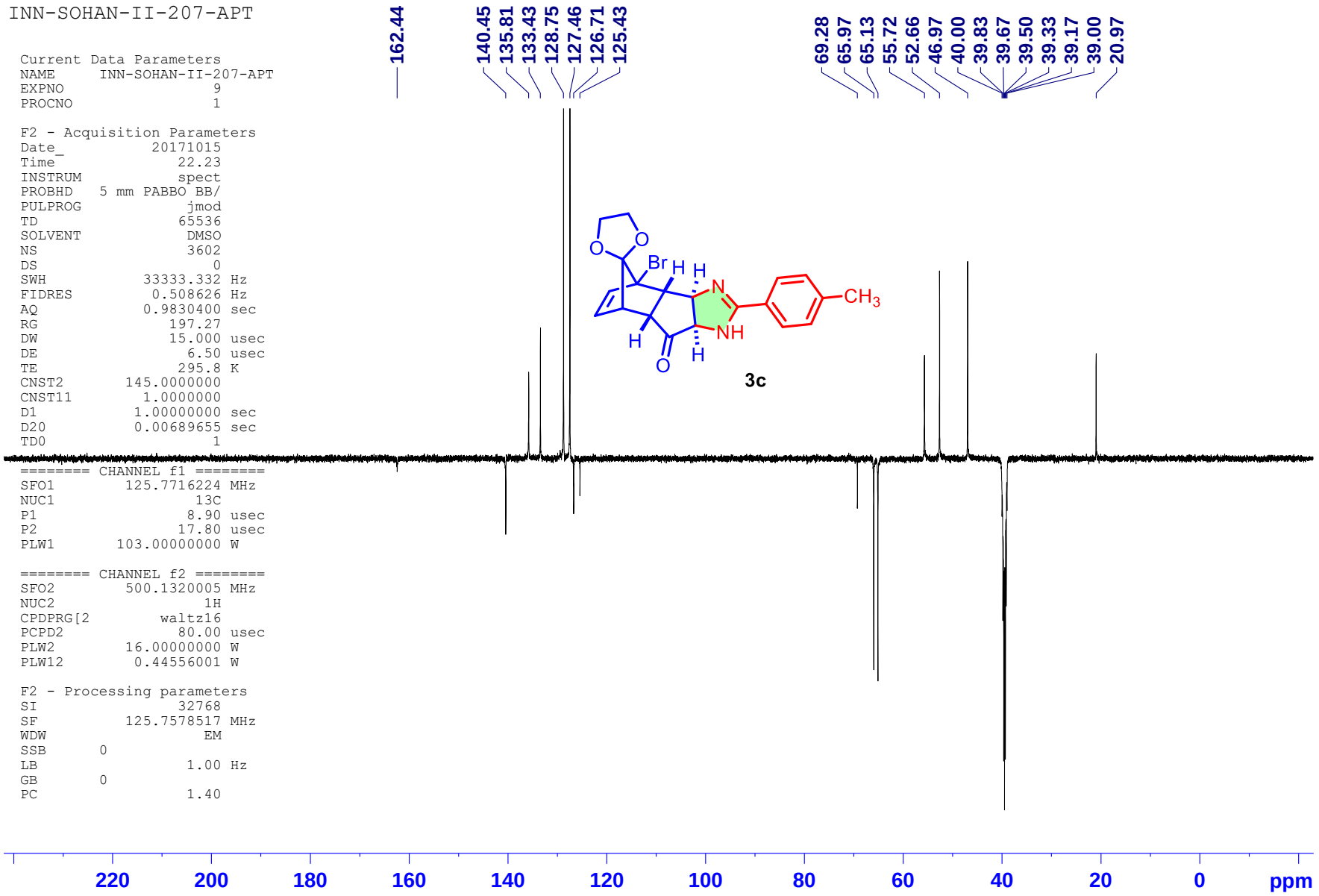
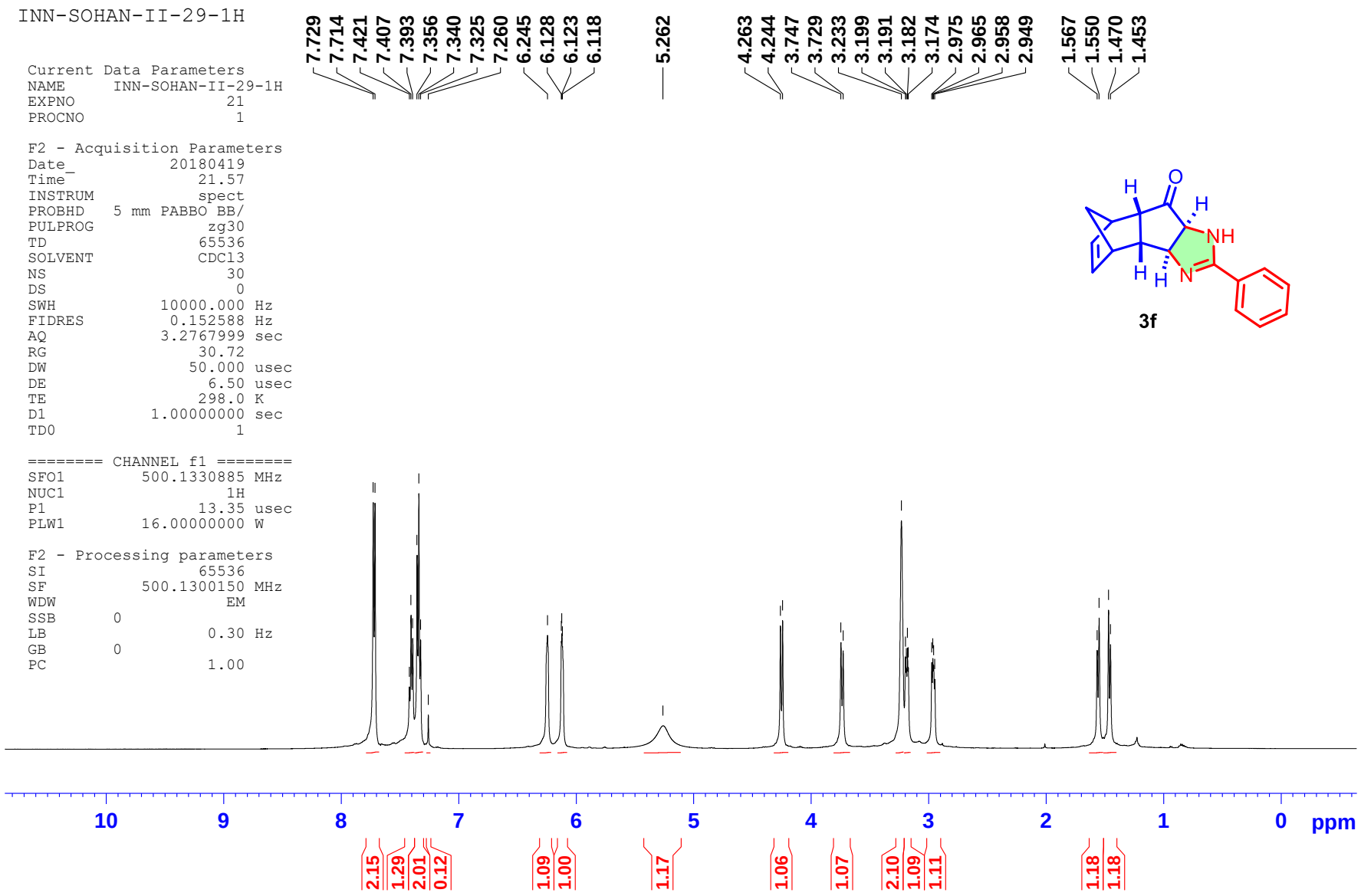


Figure S7. ^{13}C-APT NMR of compound **3c**



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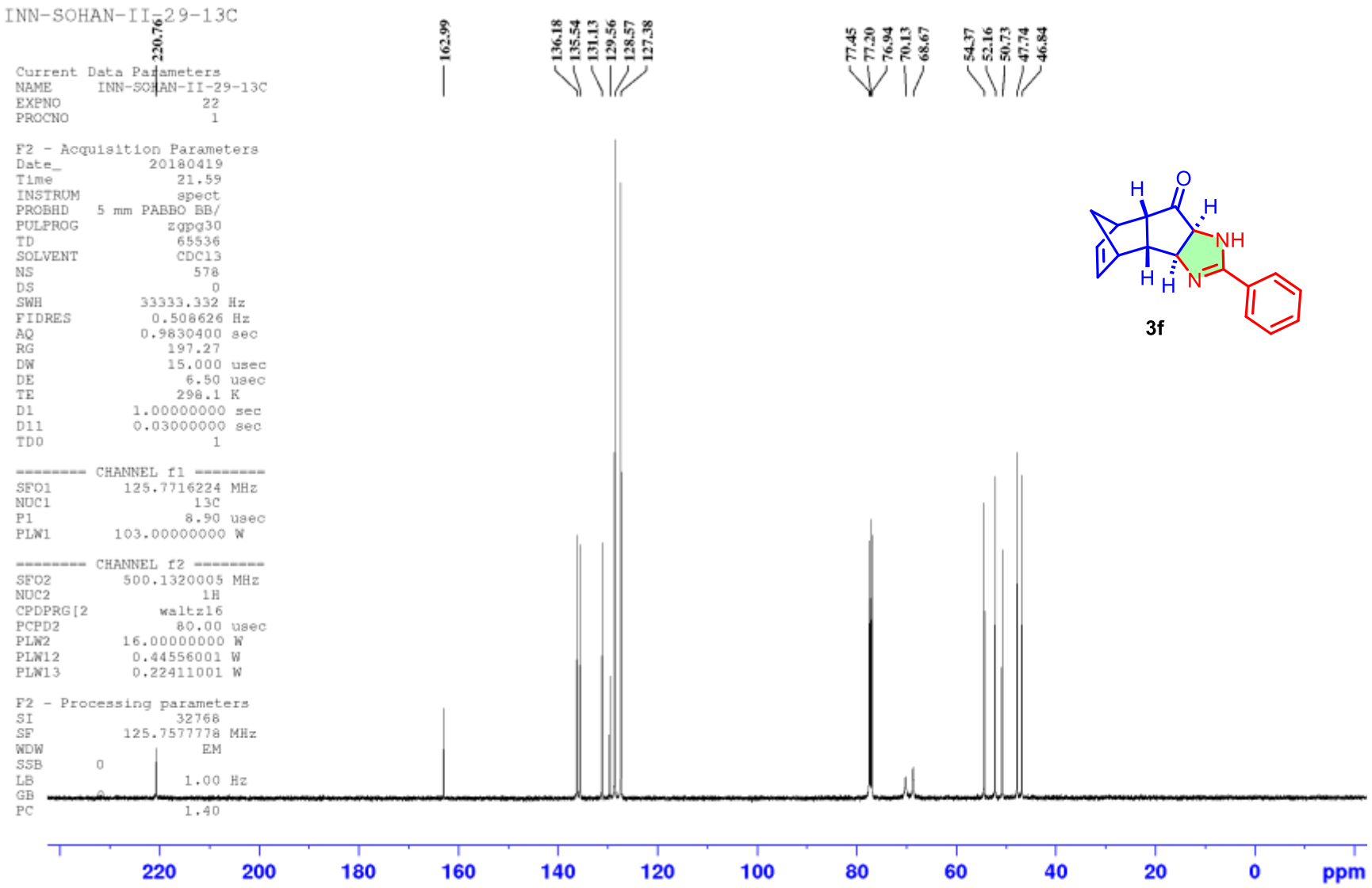
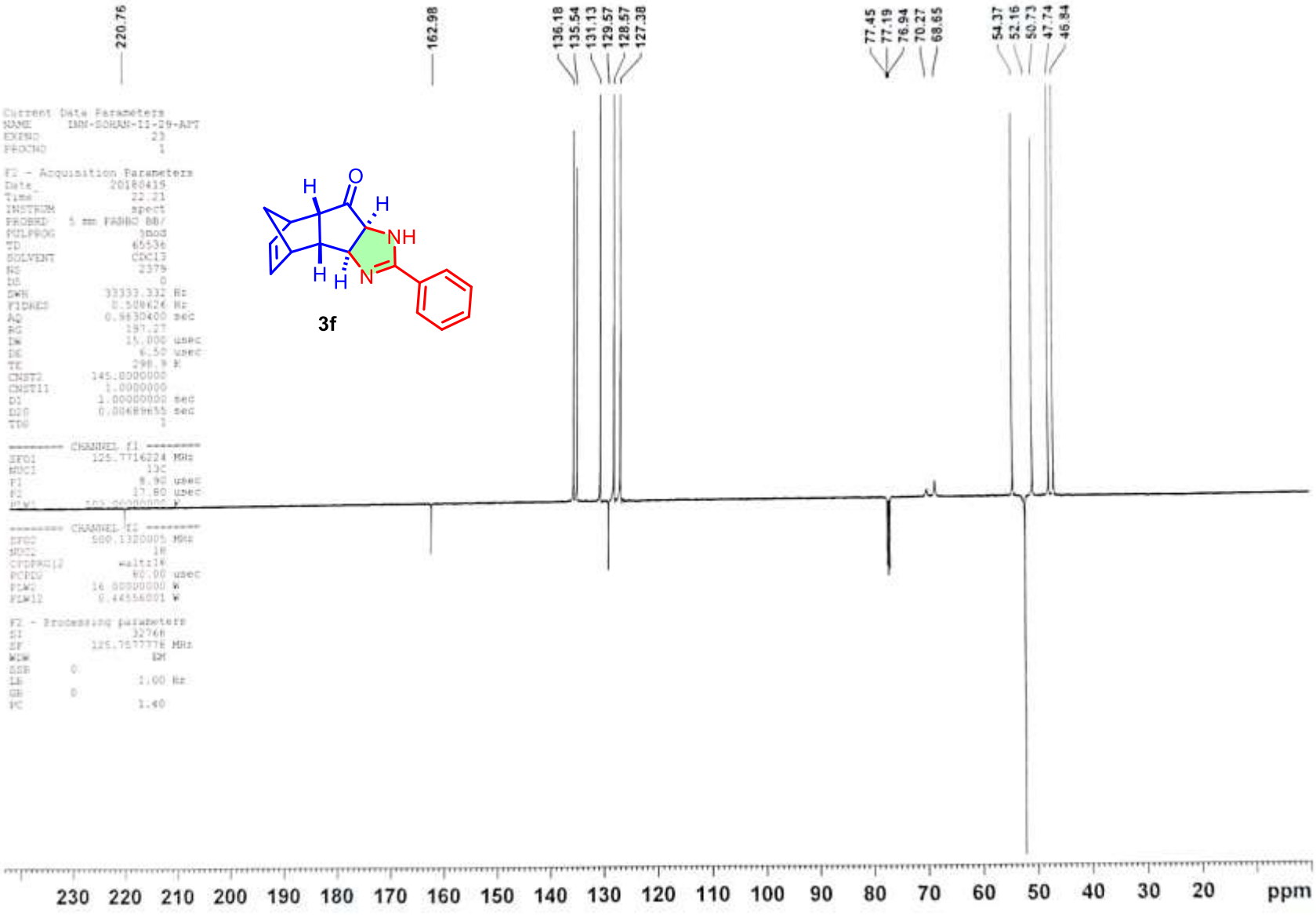


Figure S9. ^{13}C NMR of compound **3f**



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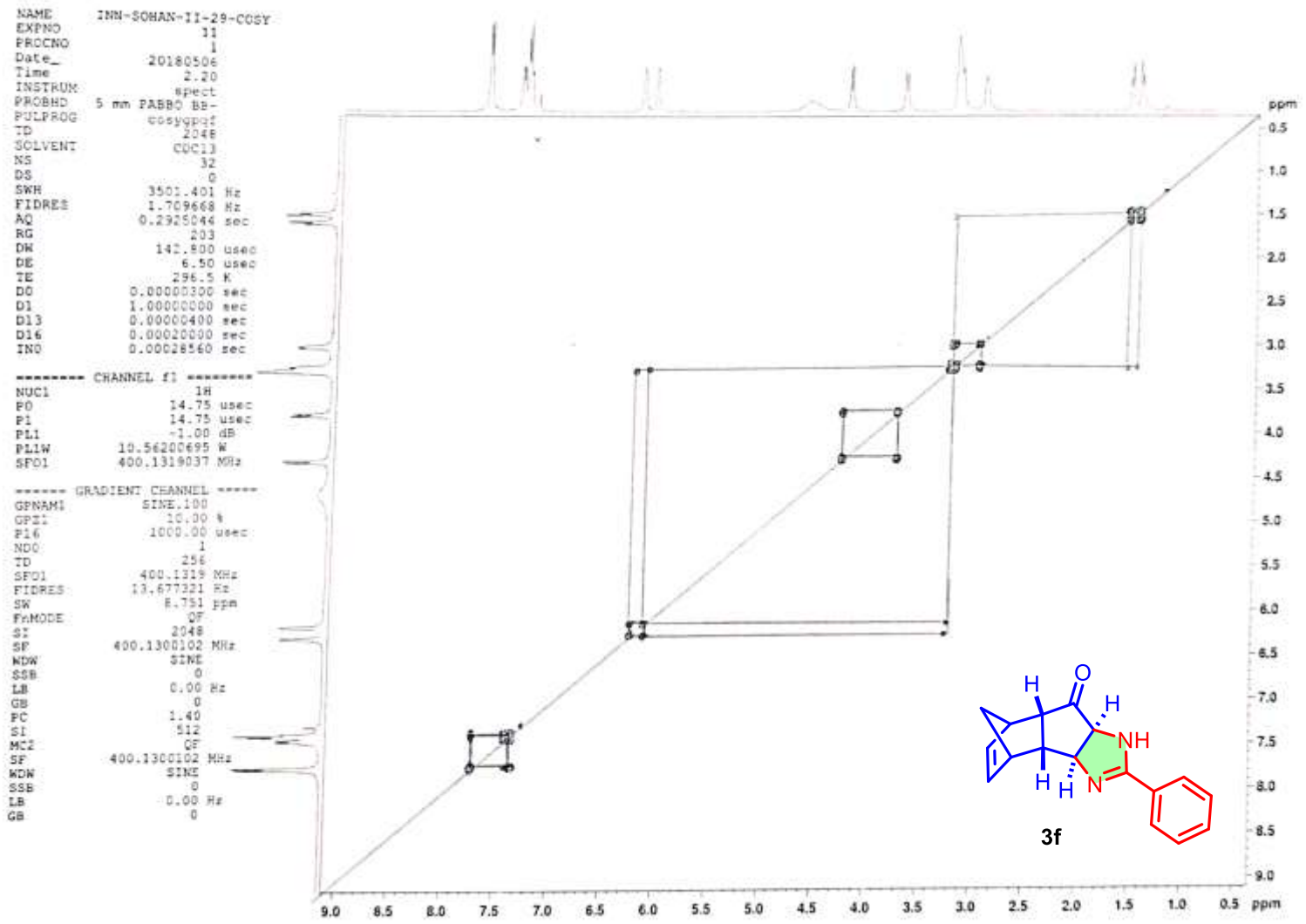

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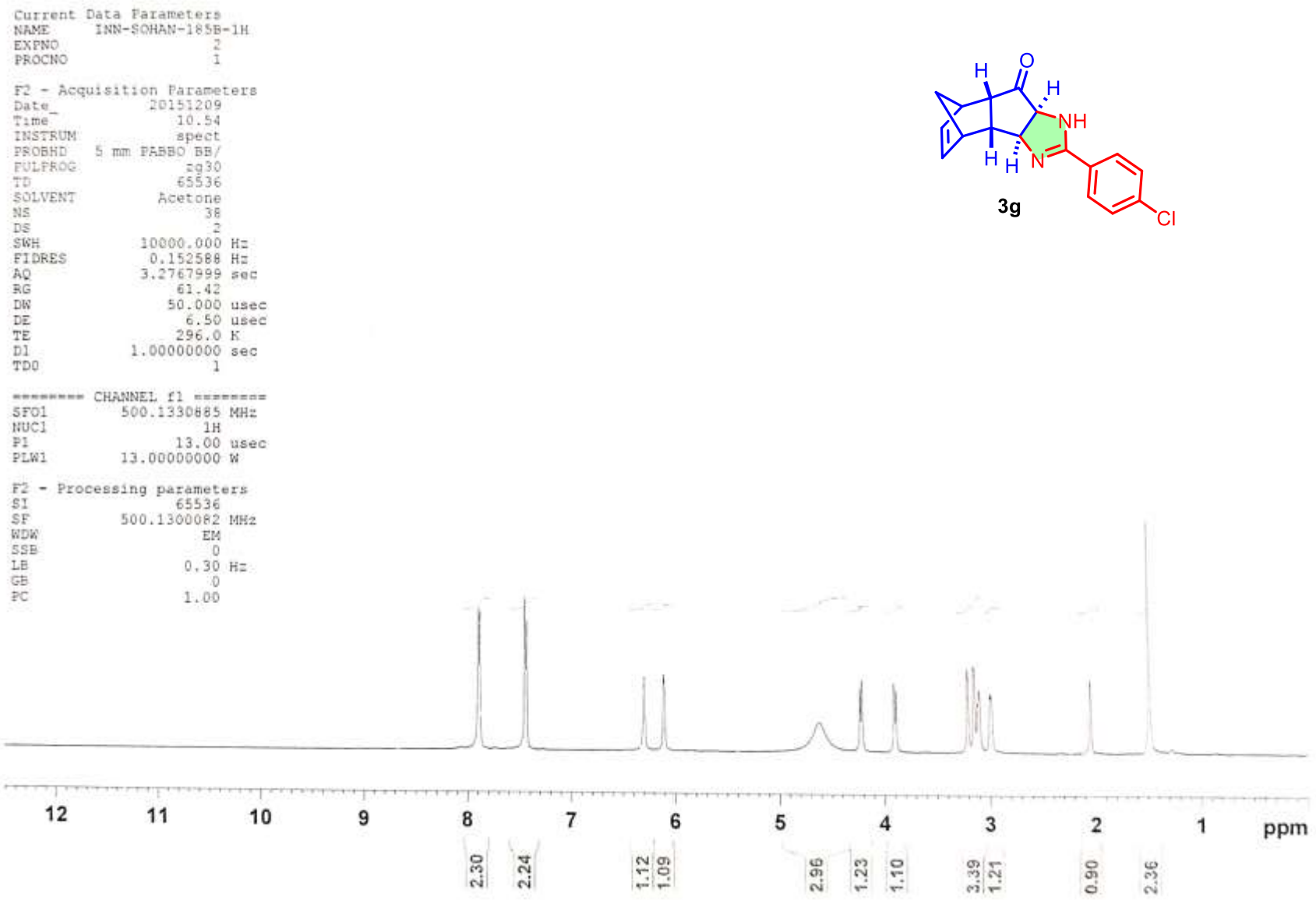

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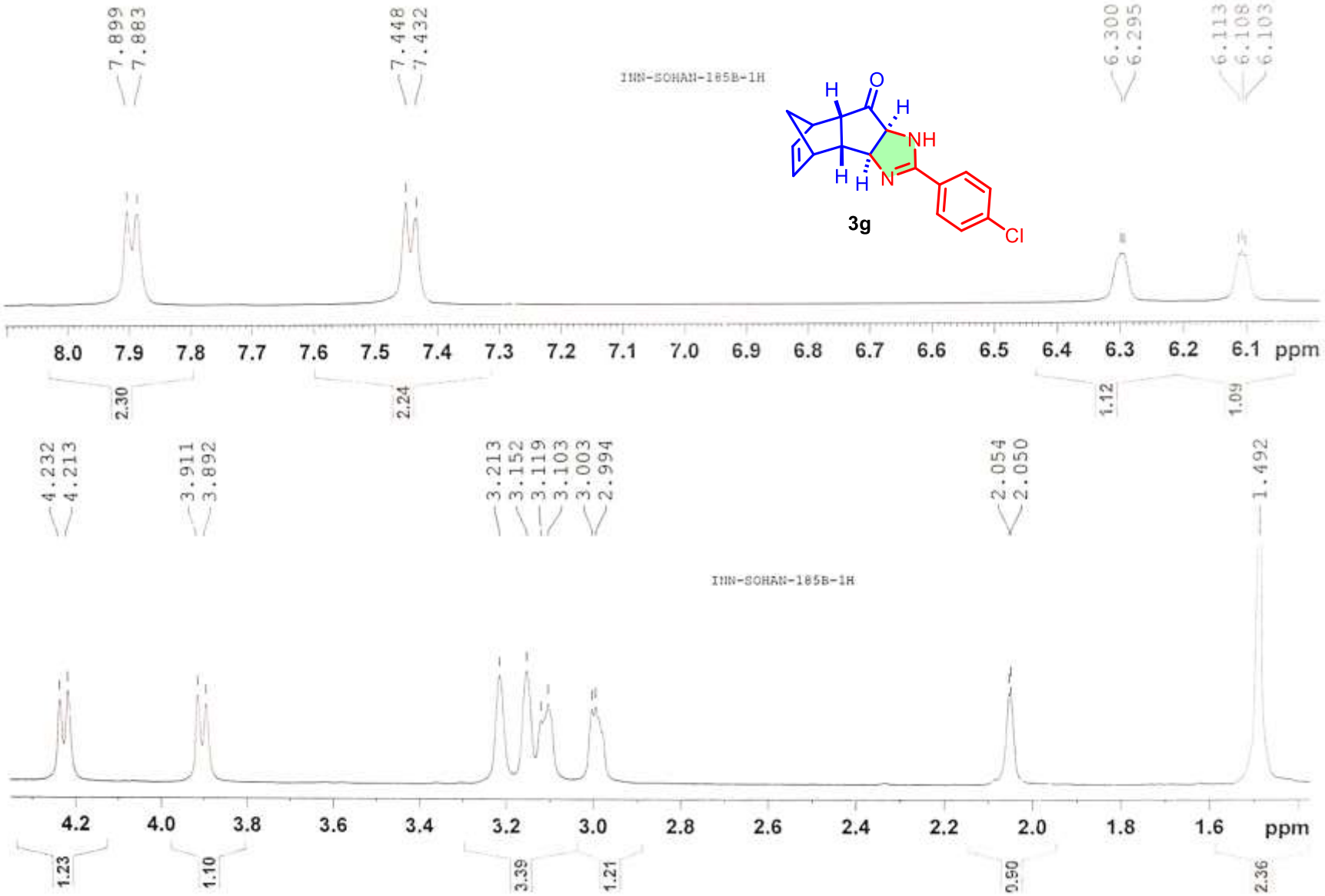
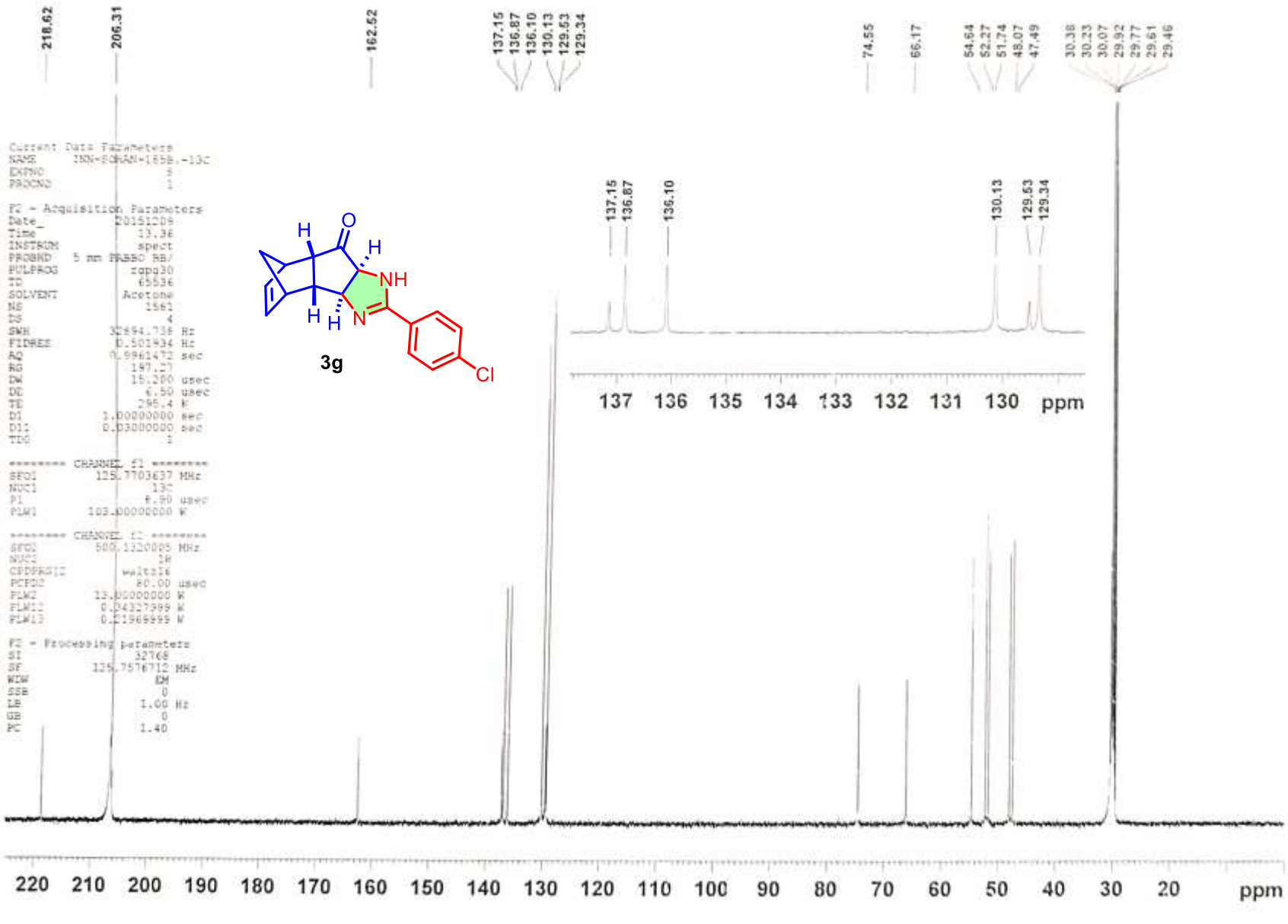


Figure S12a. ^{1}H NMR of compound **3g**



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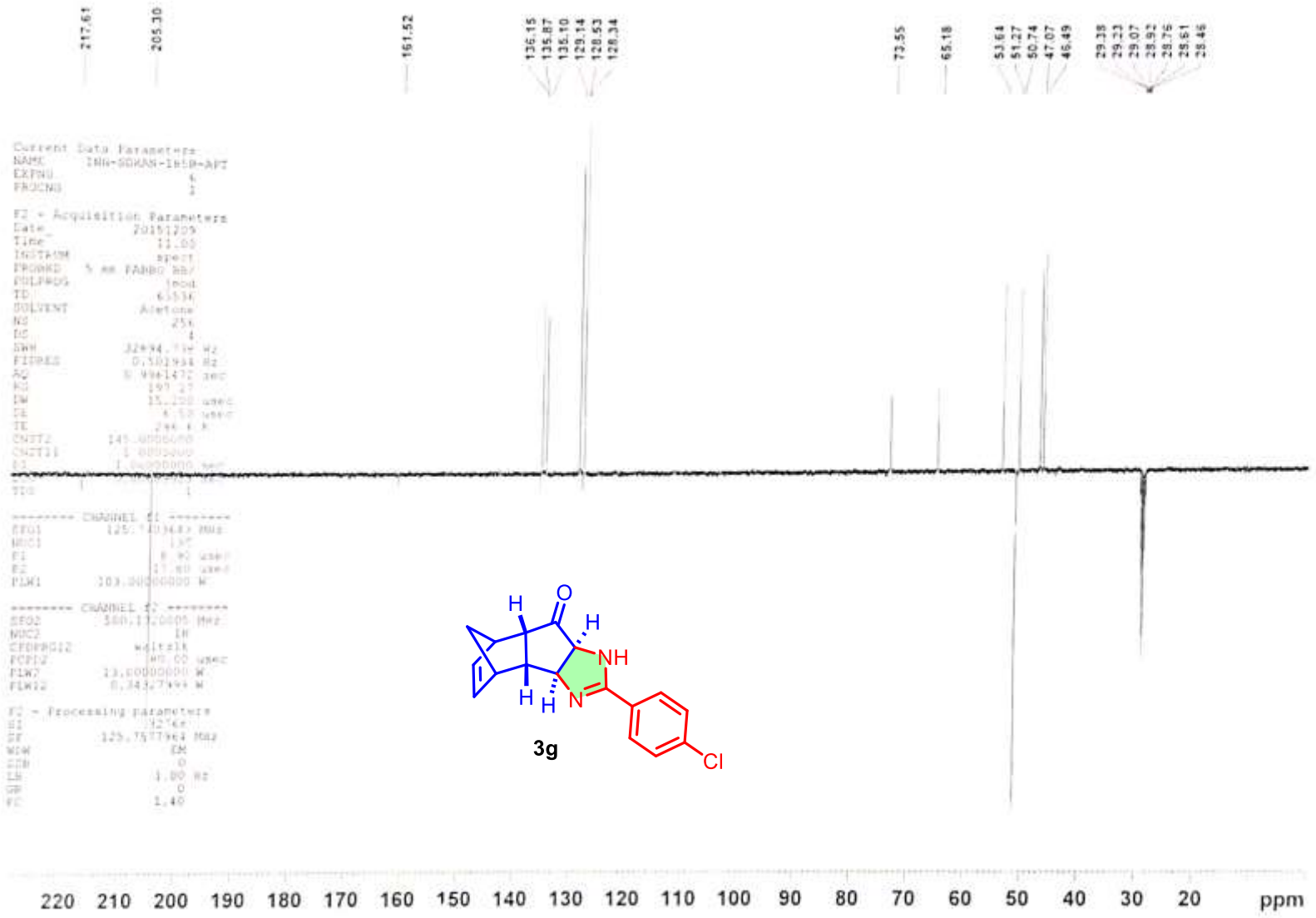

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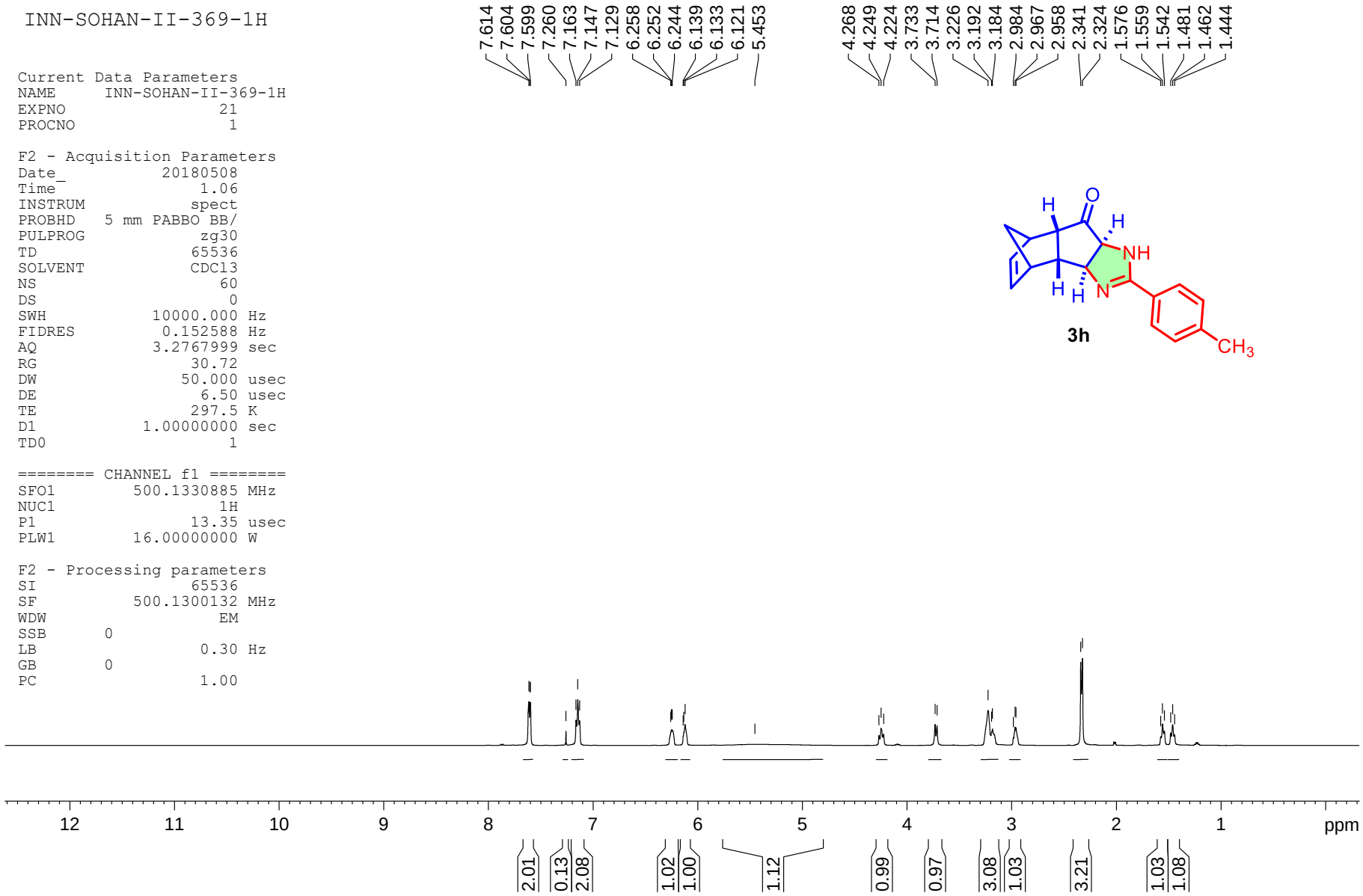

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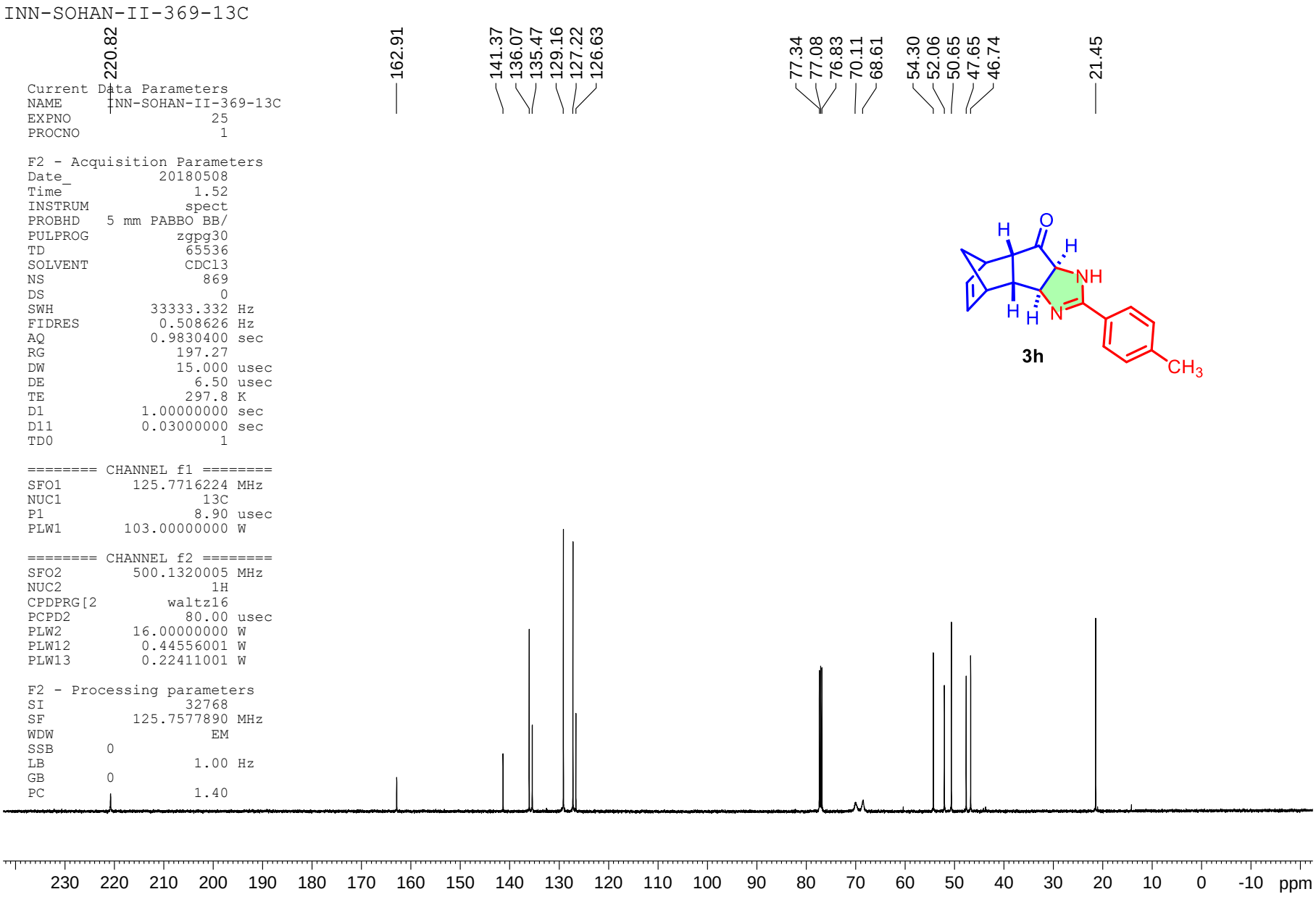

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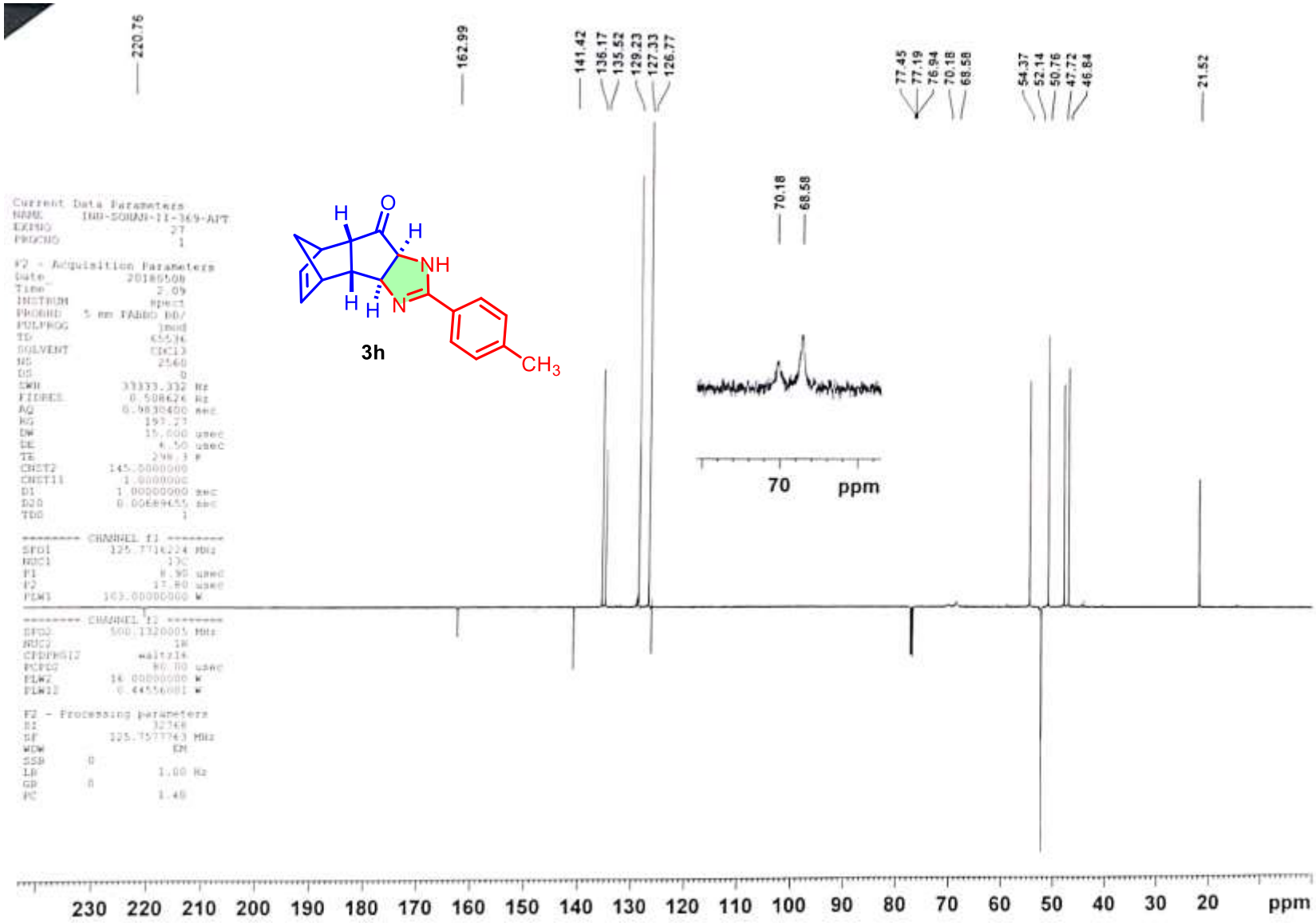

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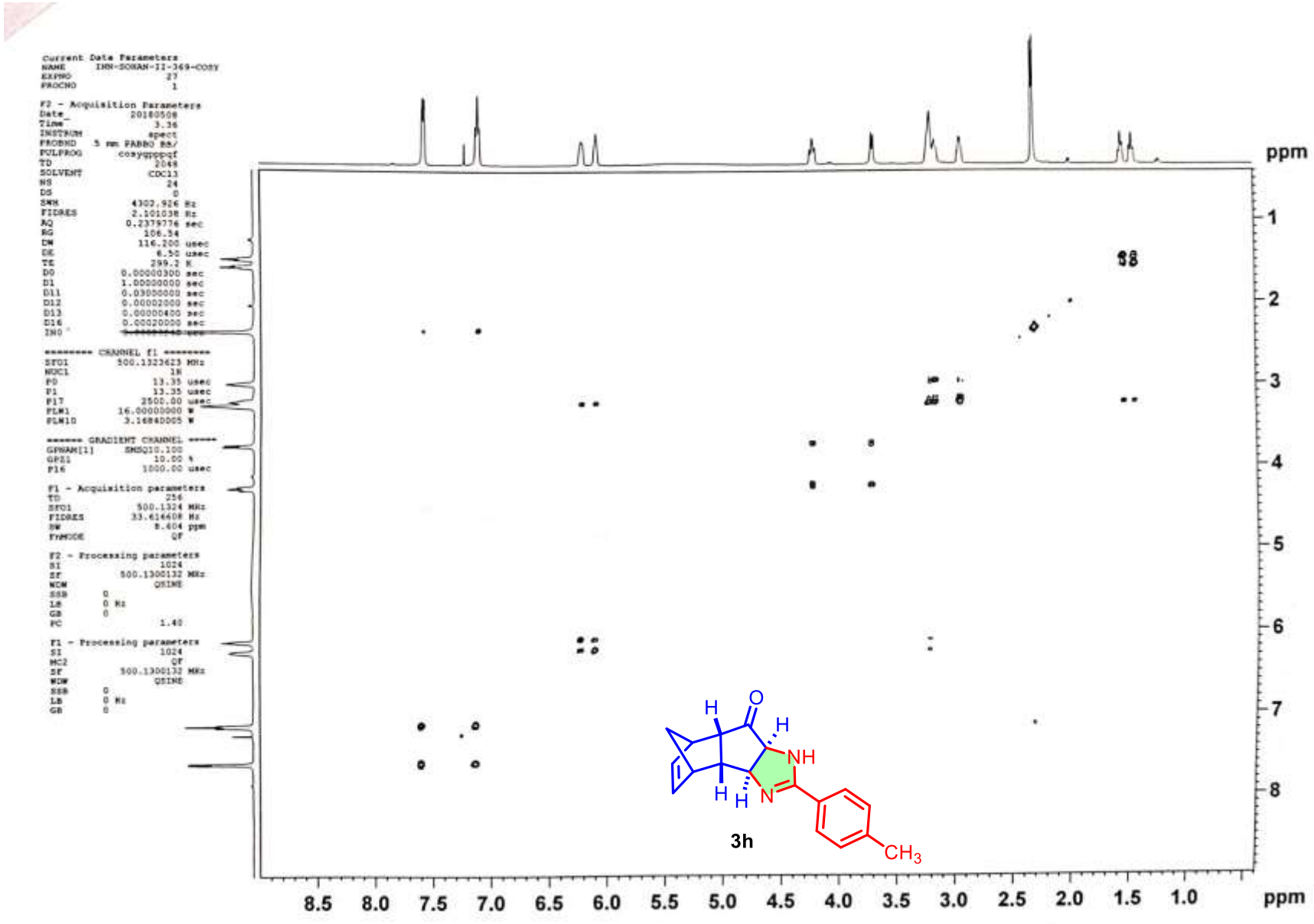


Figure S18. ^{1}H-^{1}H COSY NMR of compound **3h**

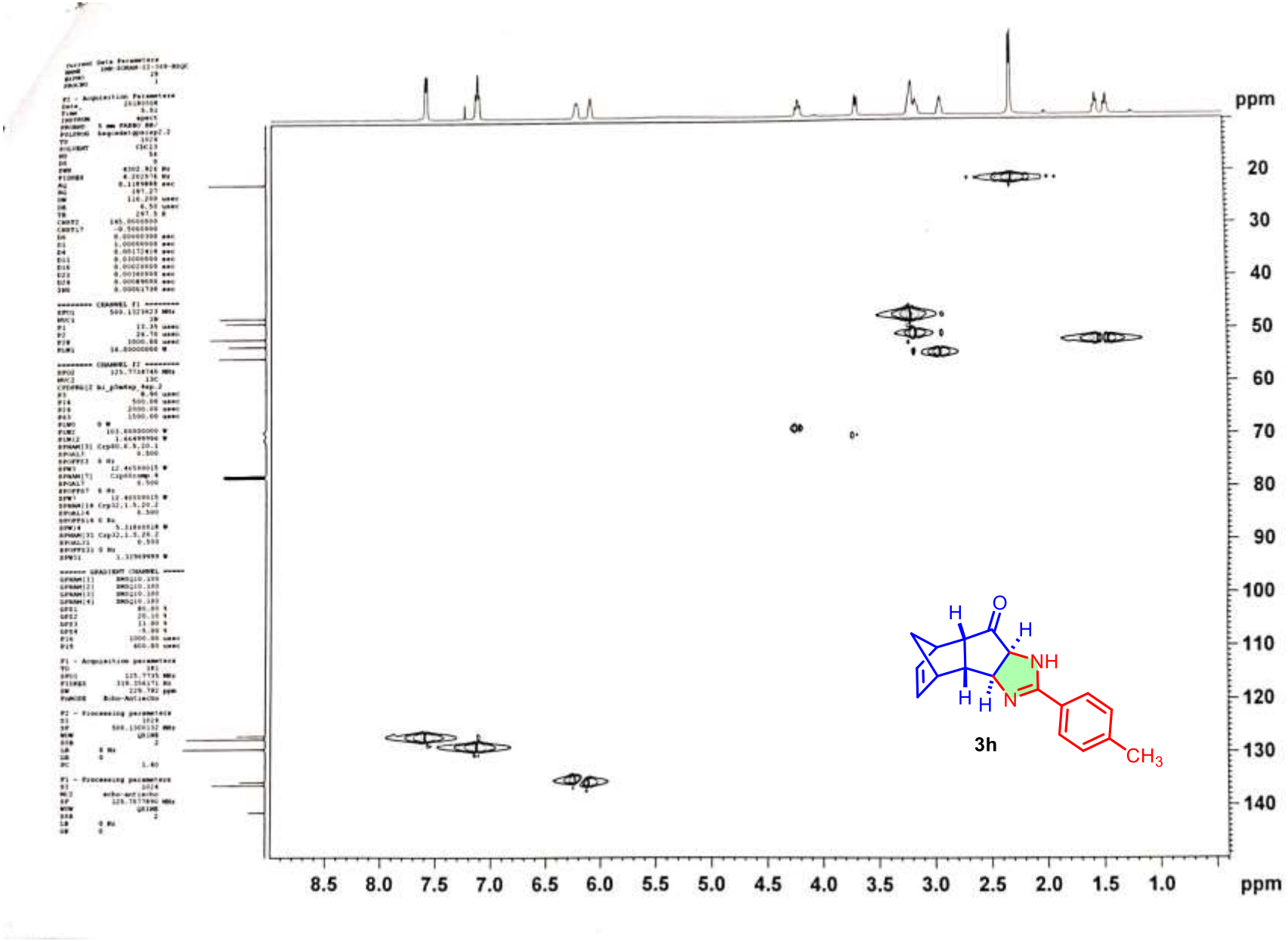


Figure S19. ^{1}H-^{13}C HSQC NMR of compound **3h**

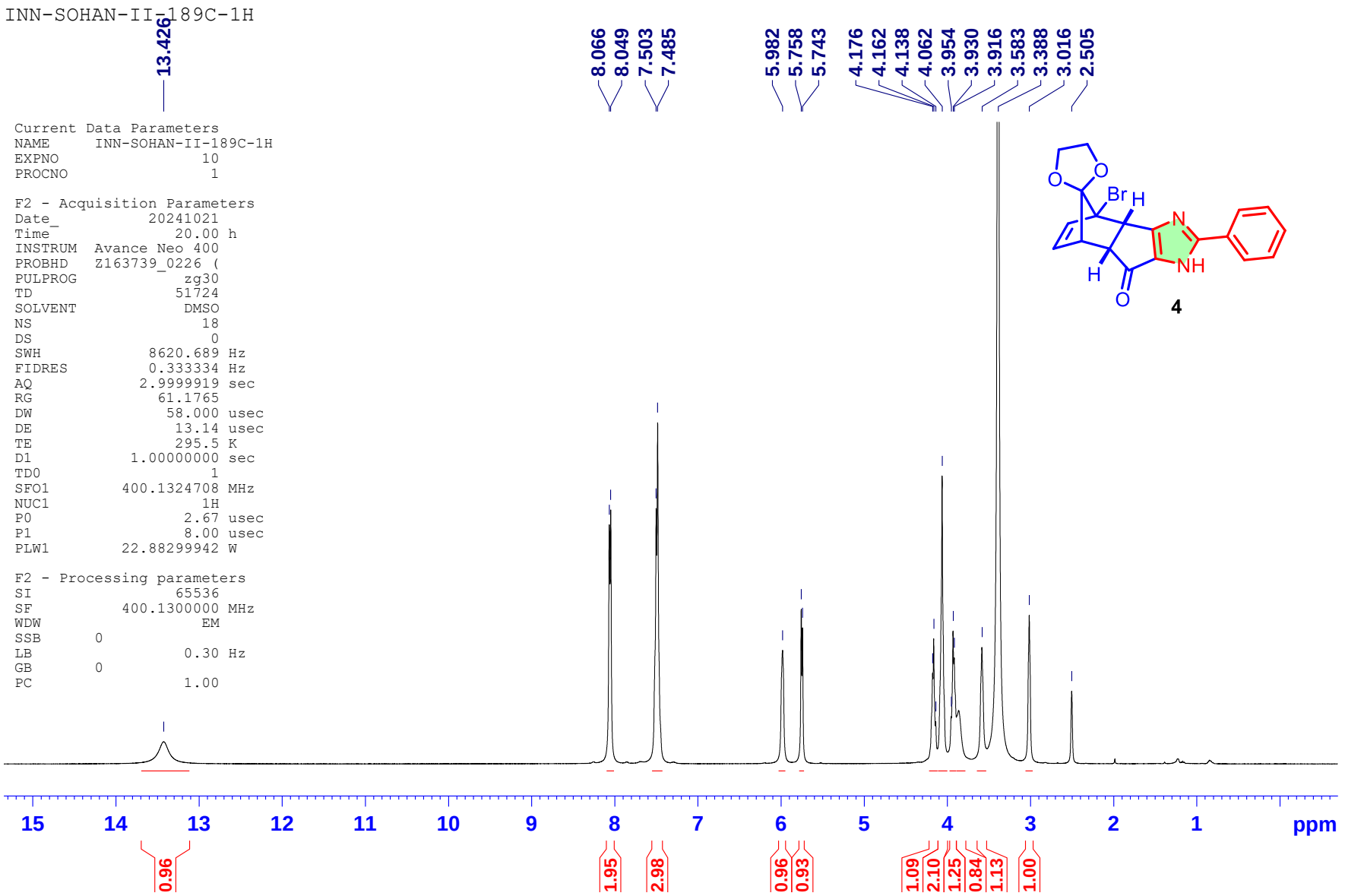


Figure S20. ^{1}H NMR of compound **4**

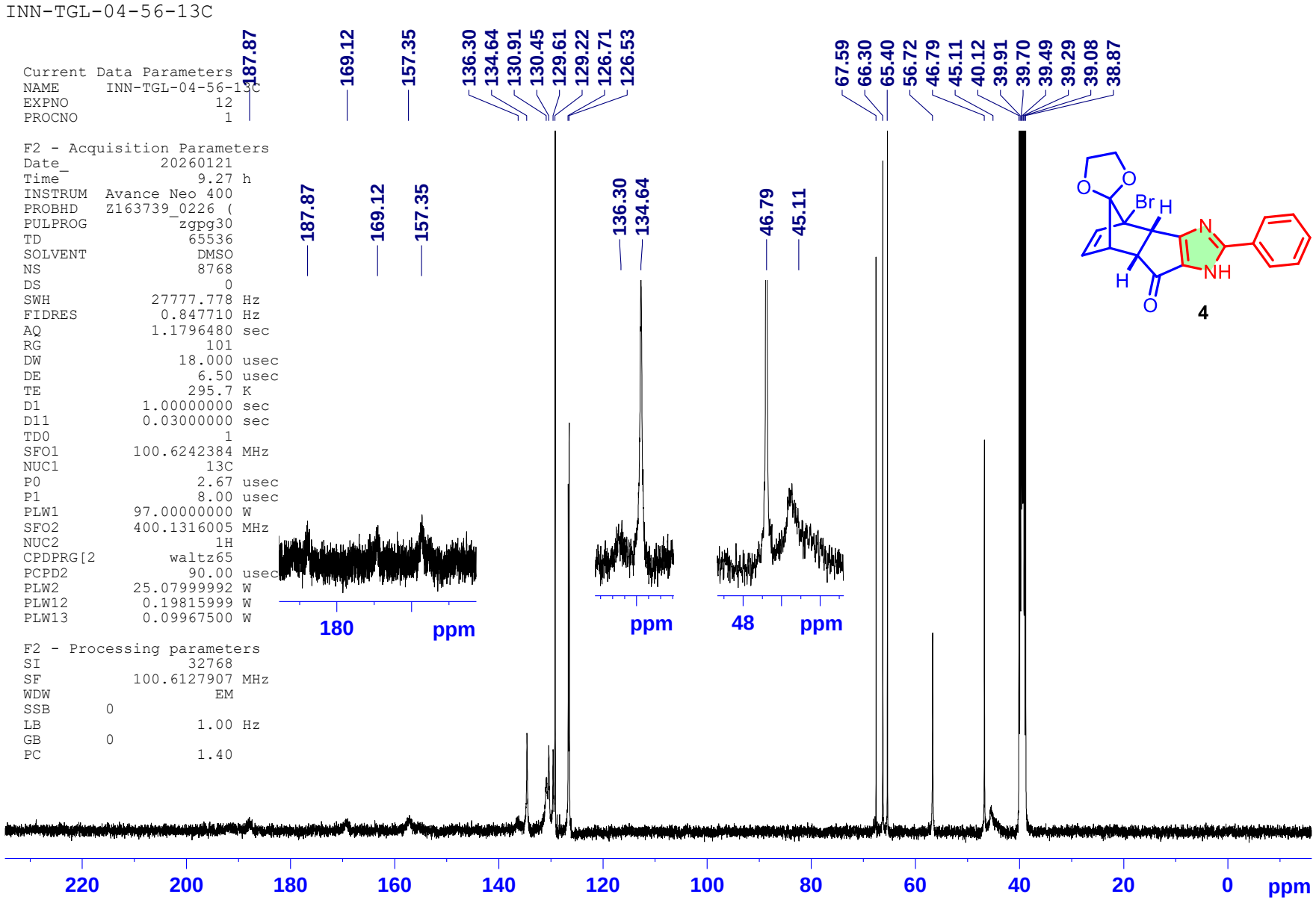


Figure S21. ^{13}C NMR of compound **4**

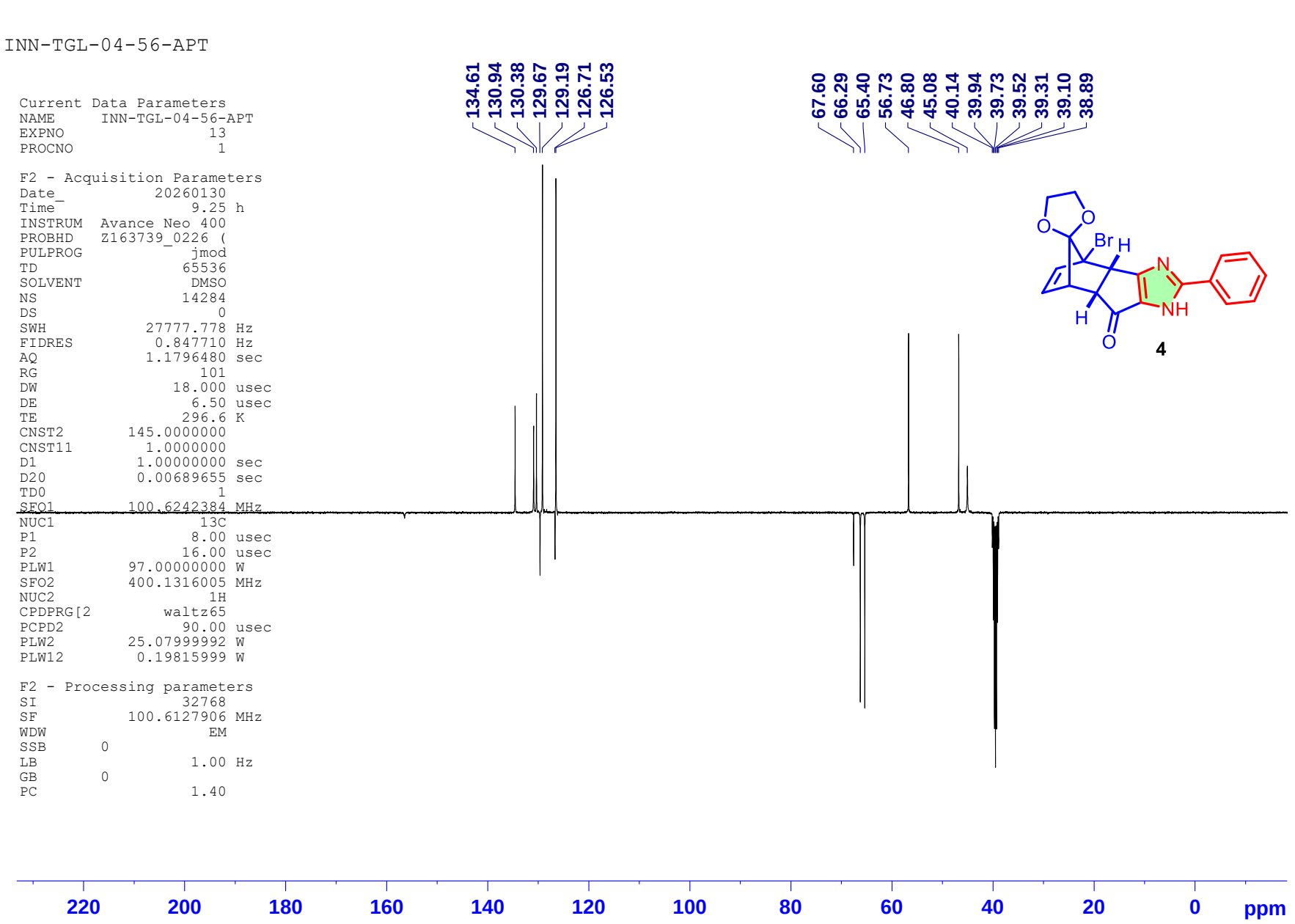


Figure S22. ^{13}C-APT NMR of compound **4**

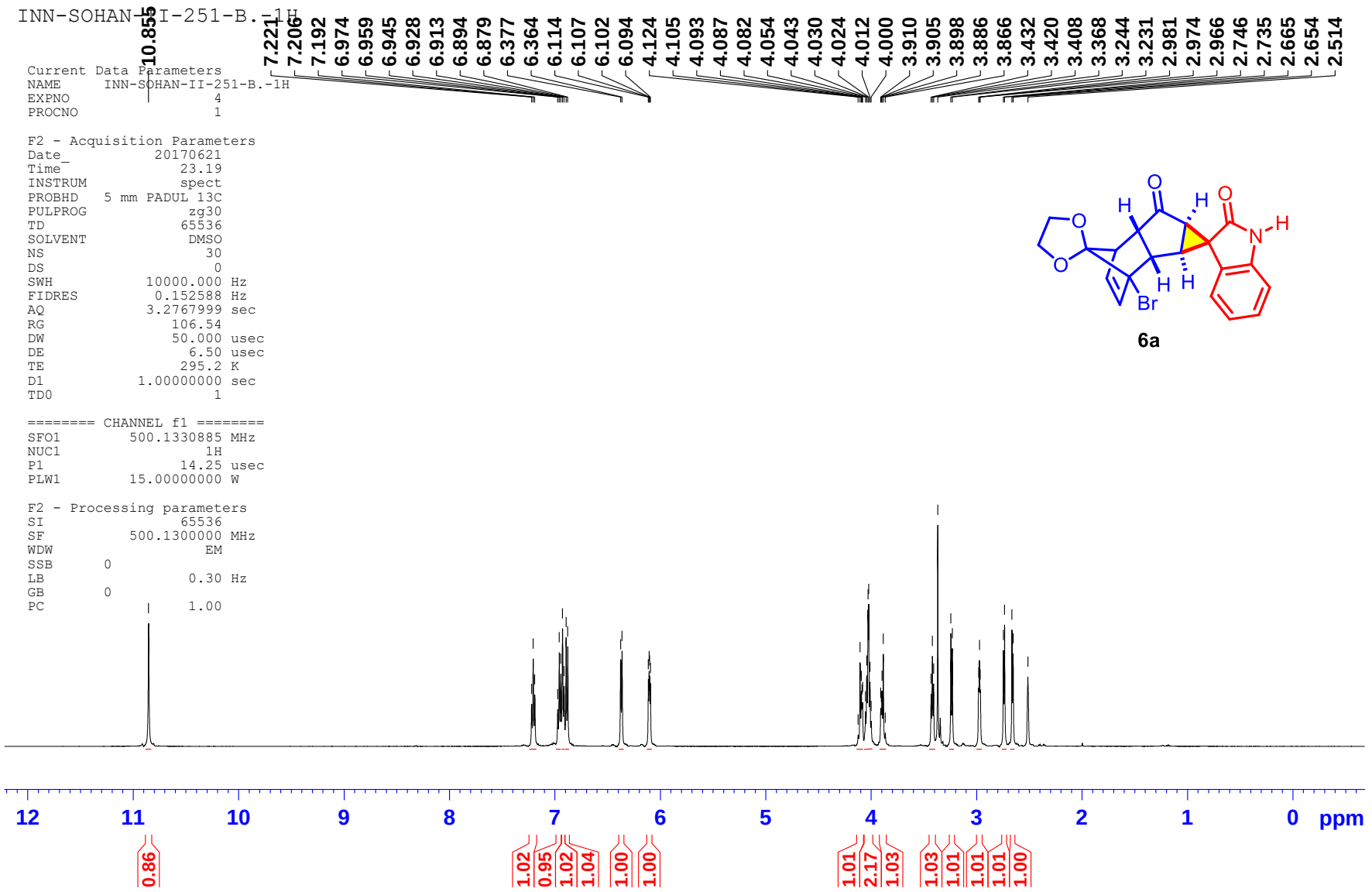
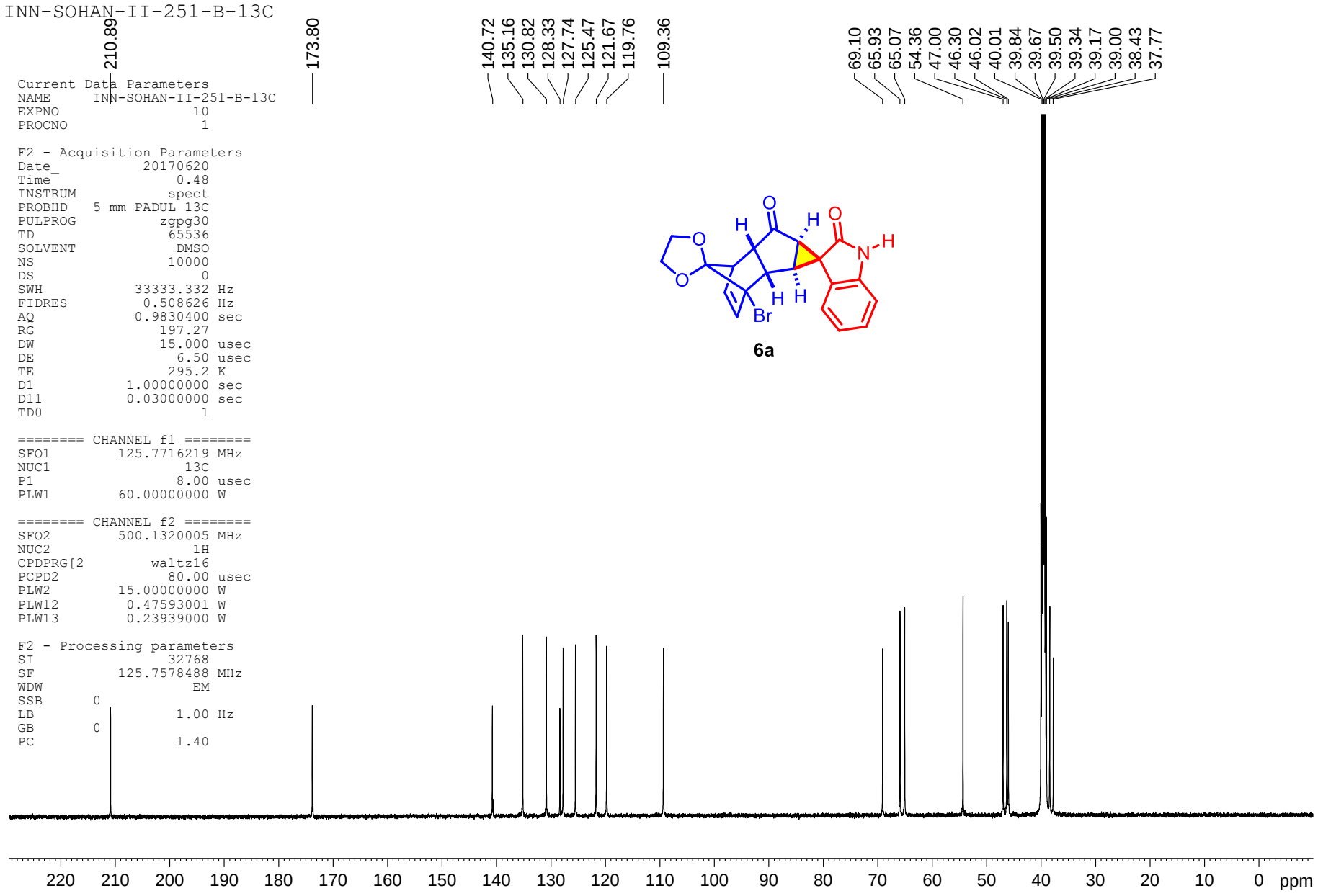


Figure S23. ^{1}H NMR of compound **6a**



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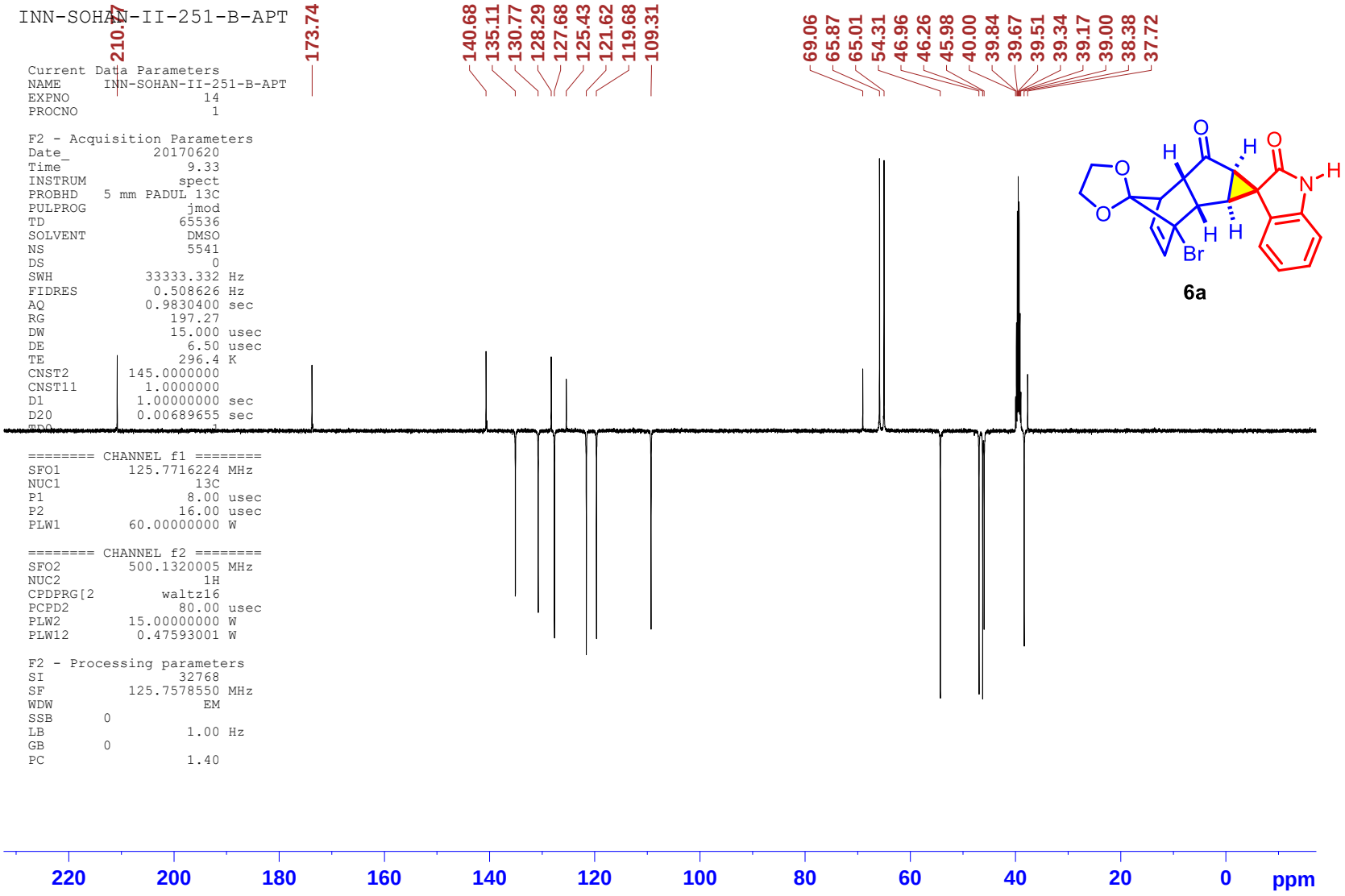
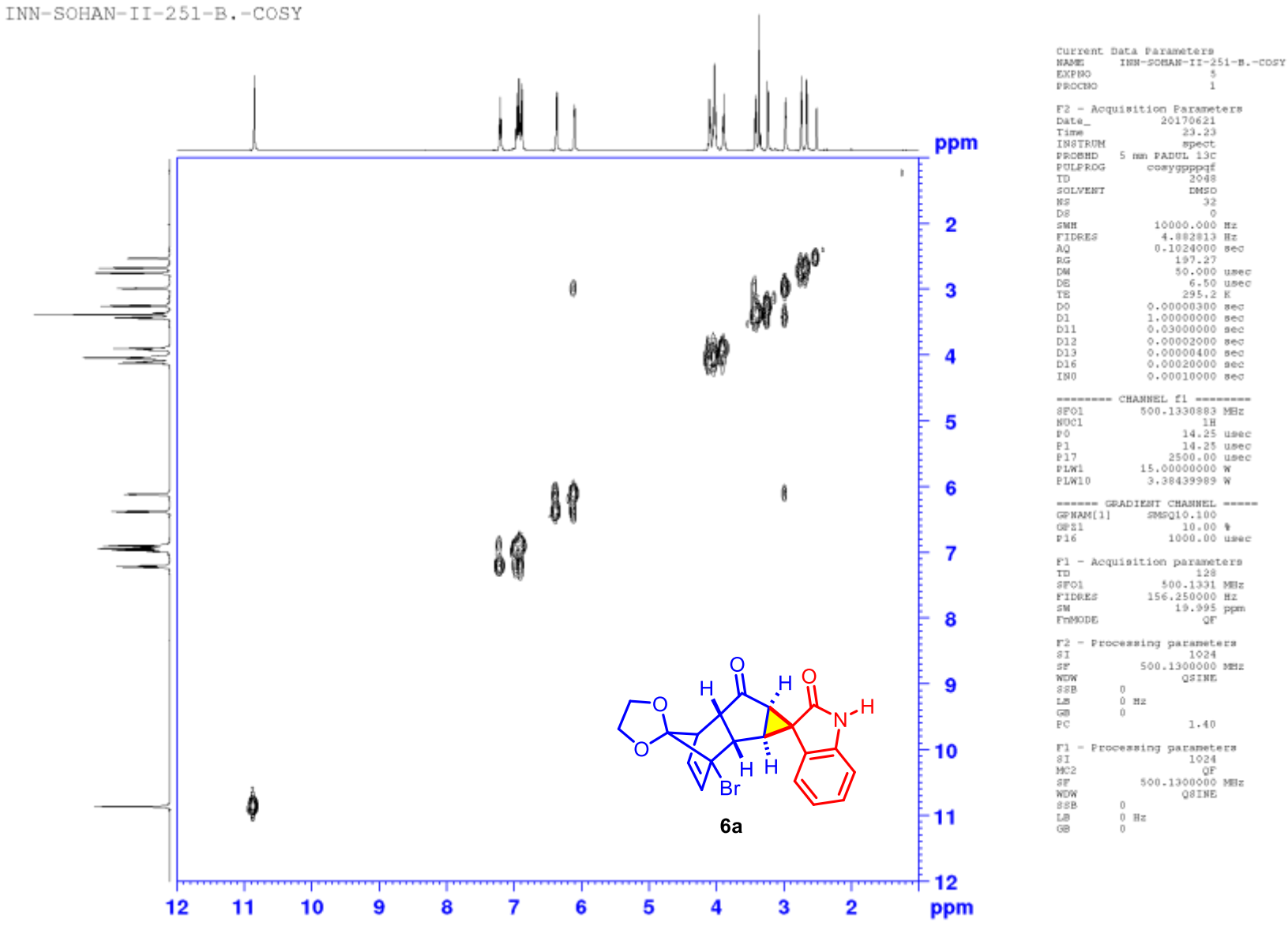


Figure S25. ^{13}C-APT NMR of compound **6a**

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SOLVENT              DMSO
NS                     32
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FIDRES               4.882813 Hz
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RG                   197.27
DW                   50.000 usec
DE                    6.50 usec
TE                   295.2 K
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D1                1.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec
D13               0.00000400 sec
D16               0.00020000 sec
IN0               0.00010000 sec

======== CHANNEL f1 ========
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NUC1                     1H
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P1                    14.25 usec
P17                 2500.00 usec
PLW1             15.00000000 W
PLW10             3.38439989 W

====== GRADIENT CHANNEL =====
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GPZ1                 10.00 %
P16                1000.00 usec

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FnMODE                   QF

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LB           0 Hz
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F1 - Processing parameters
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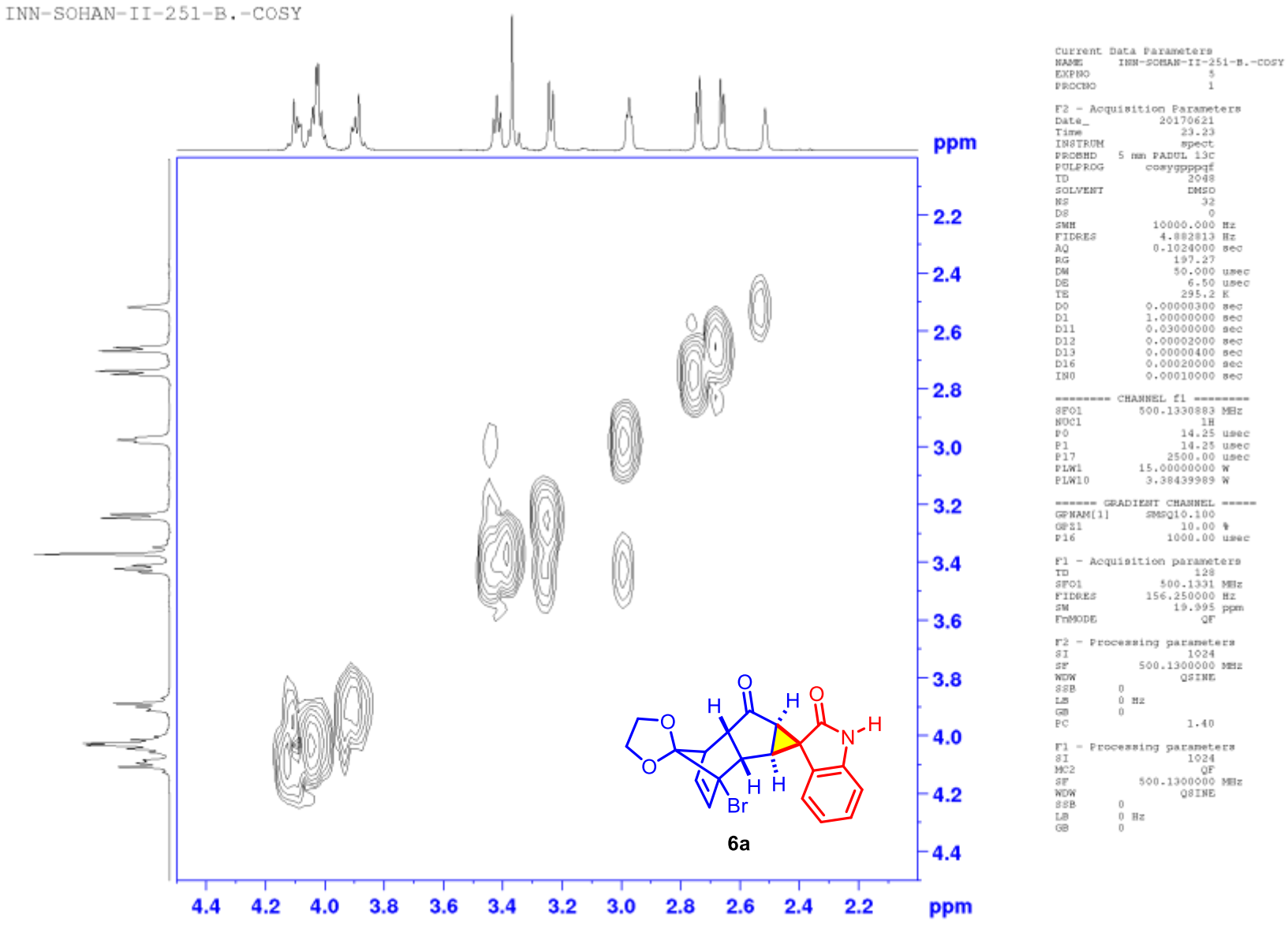
Figure S26. ^{1}H-^{1}H COSY NMR of compound **6a**

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TD                   2048
SOLVENT              DMSO
NS                     32
DS                      0
SWH              10000.000 Hz
FIDRES           4.882813 Hz
AQ               0.1024000 sec
RG                  197.27
DW                  50.000 usec
DE                   6.50 usec
TE                  295.2 K
D0               0.00000300 sec
D1               1.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
D13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00010000 sec

======== CHANNEL f1 ========
SFO1          500.1330883 MHz
NUC1                    1H
P0                   14.25 usec
P1                   14.25 usec
P17                2500.00 usec
PLW1          15.00000000 W
PLW10          3.38439989 W

====== GRADIENT CHANNEL =====
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GPZ1                10.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
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SFO1              500.1331 MHz
FIDRES           156.250000 Hz
SW                   19.995 ppm
FnMODE                   QF

F2 - Processing parameters
SI                       1024
SF             500.1300000 MHz
WDW                    QSINE
SSB          0
LB           0 Hz
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F1 - Processing parameters
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Figure S26a. Expansion of ^{1}H-^{1}H COSY NMR of compound **6a**

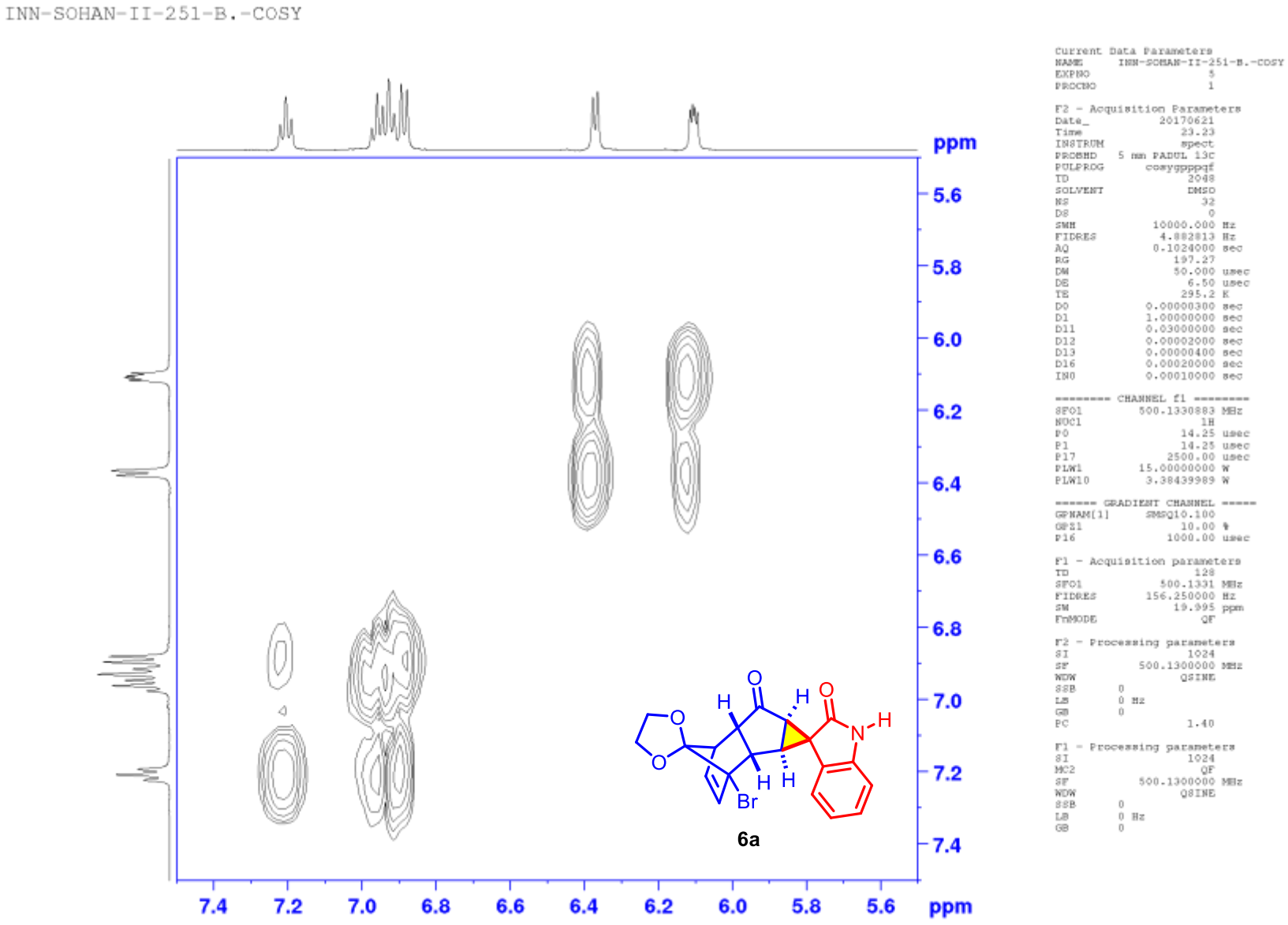


Figure S26b. Expansion of ^{1}H-^{1}H COSY NMR of compound **6a**

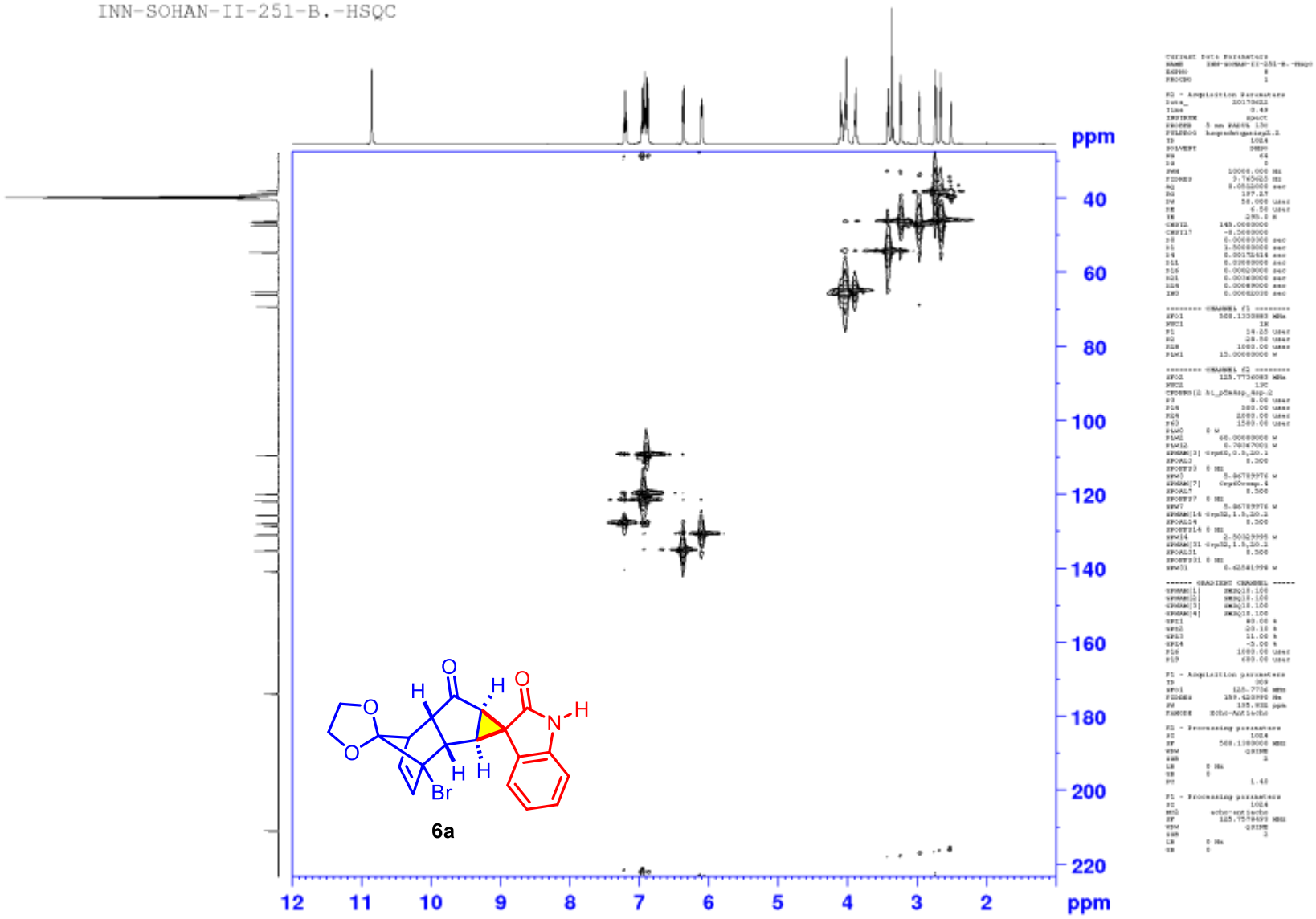


Figure S27. ^{1}H-^{13}C HSQC NMR of compound **6a**

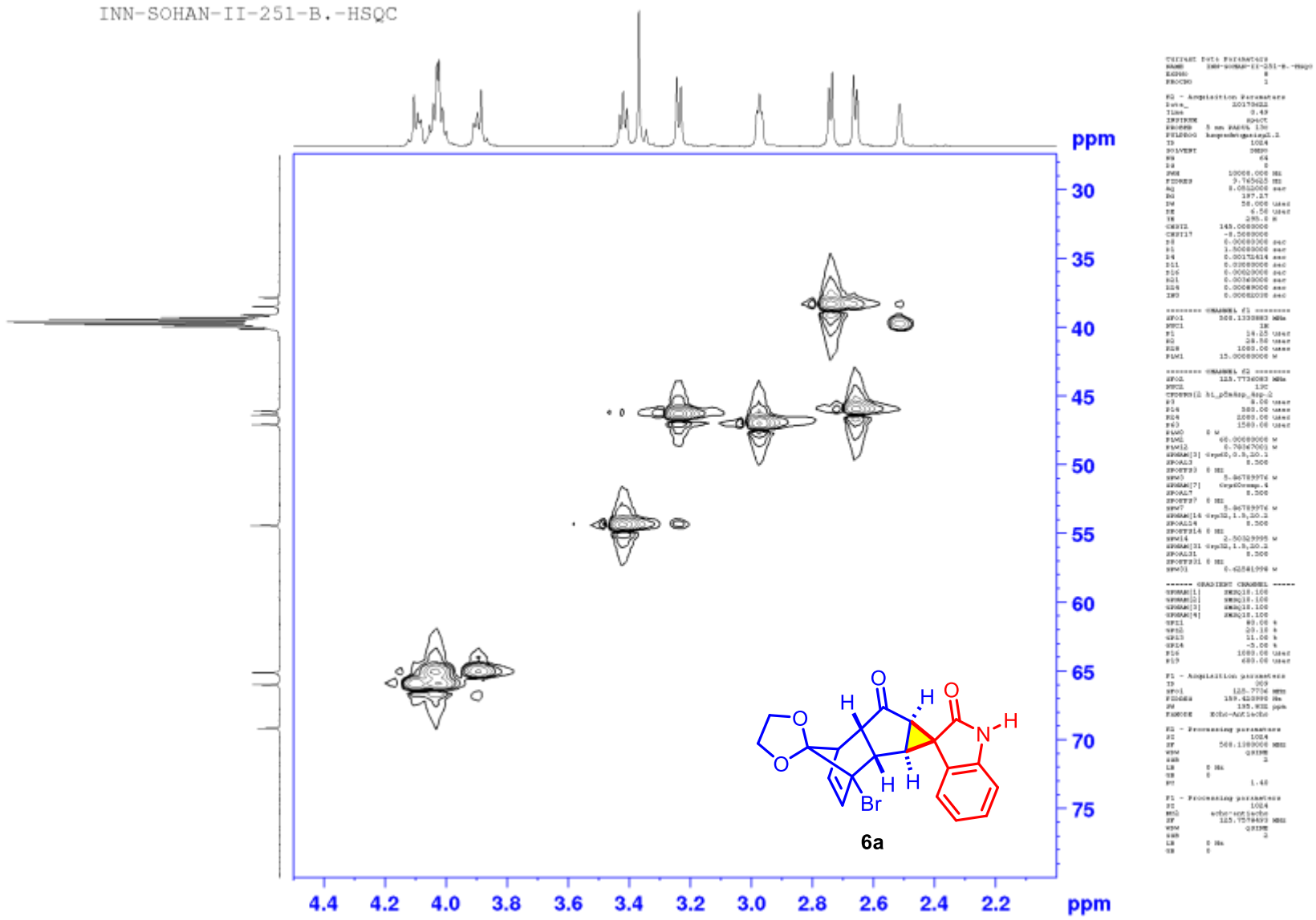


Figure S27a. Expansion of ^{1}H-^{13}C HSQC of compound **6a**

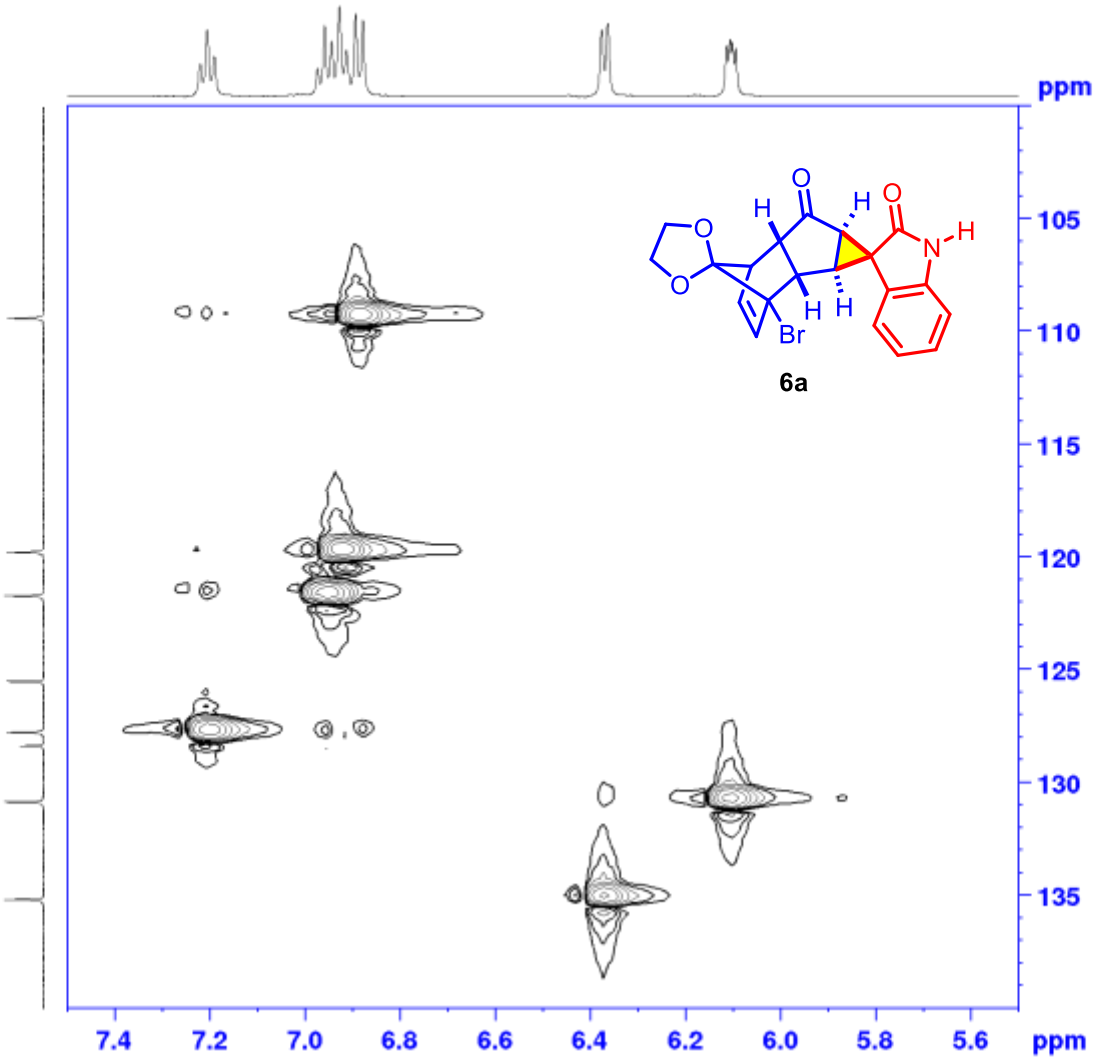


Figure S27b. Expansion of ^{1}H-^{13}C HSQC of compound **6a**

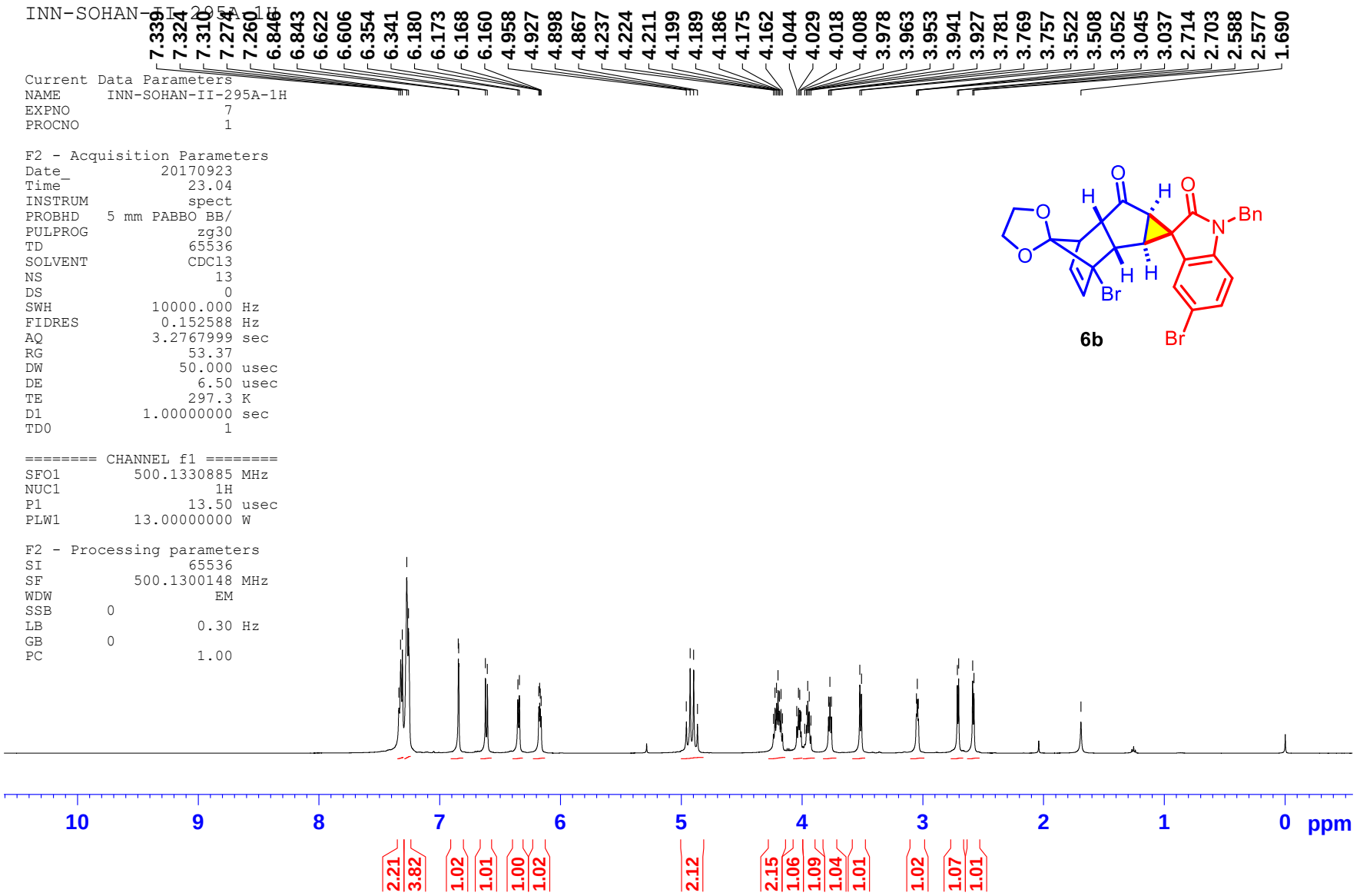


Figure S28. ^{1}H NMR of compound **6b**

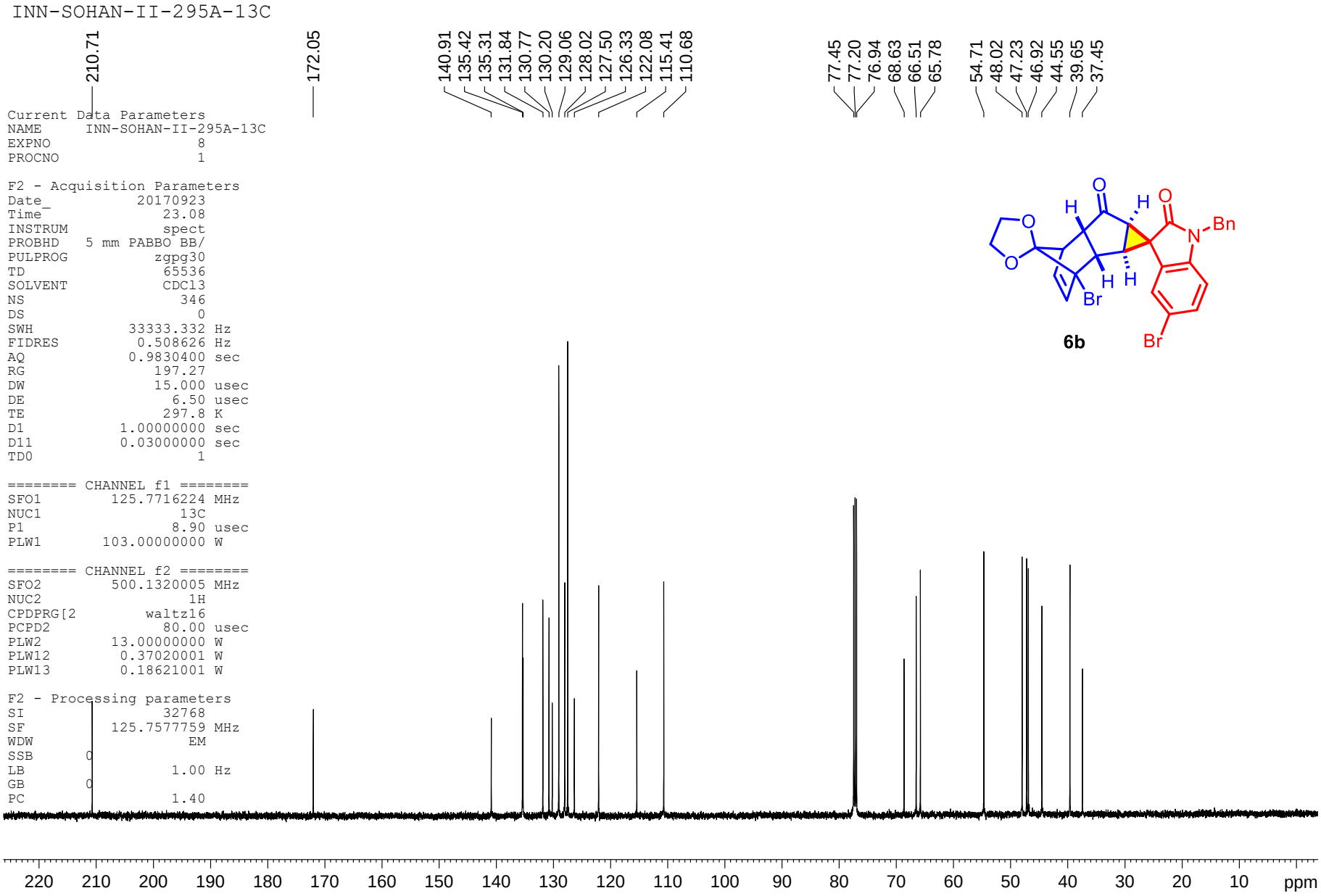


Figure S29. ^{13}C NMR of compound **6b**

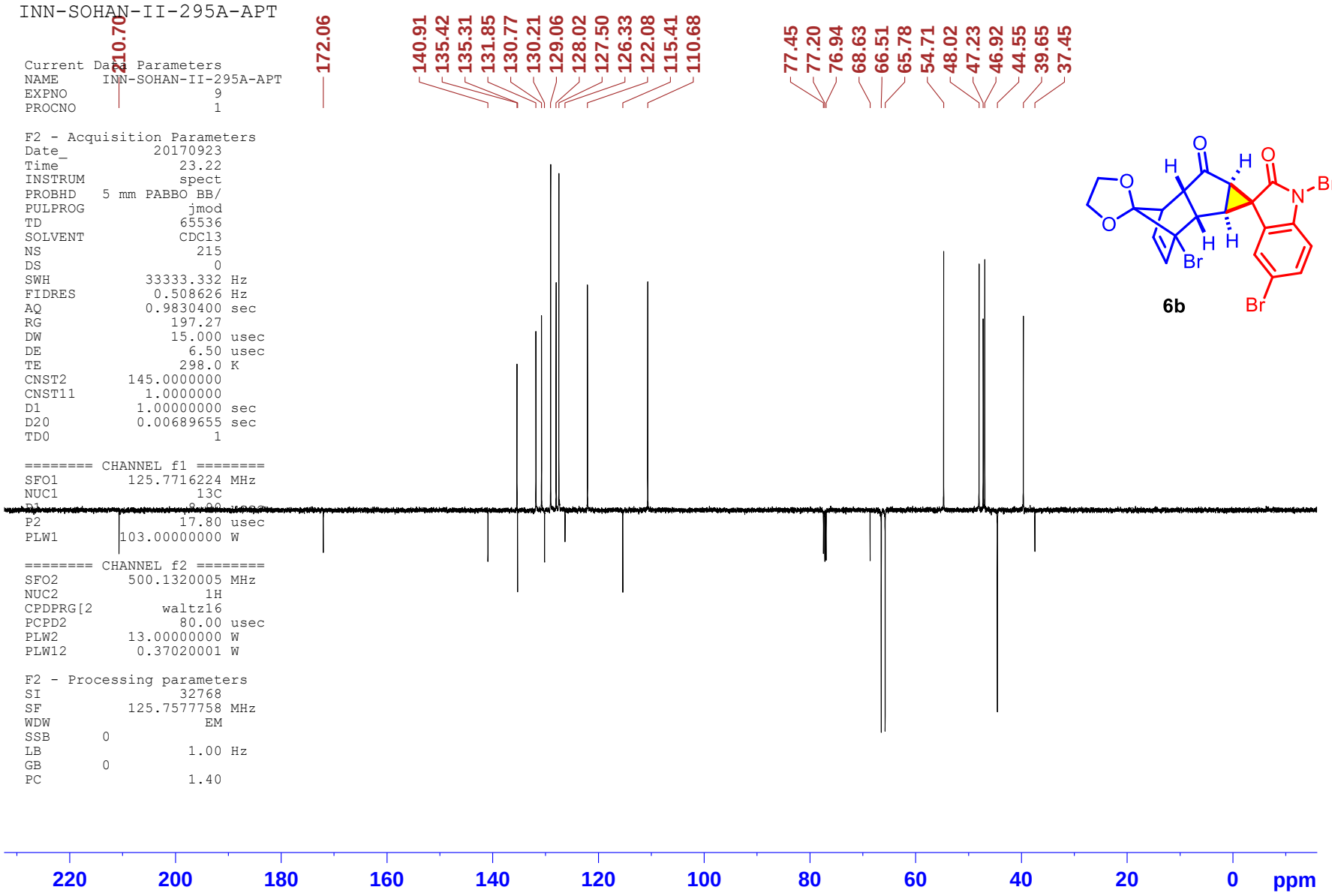


Figure S30. ^{13}C-APT NMR of compound **6b**

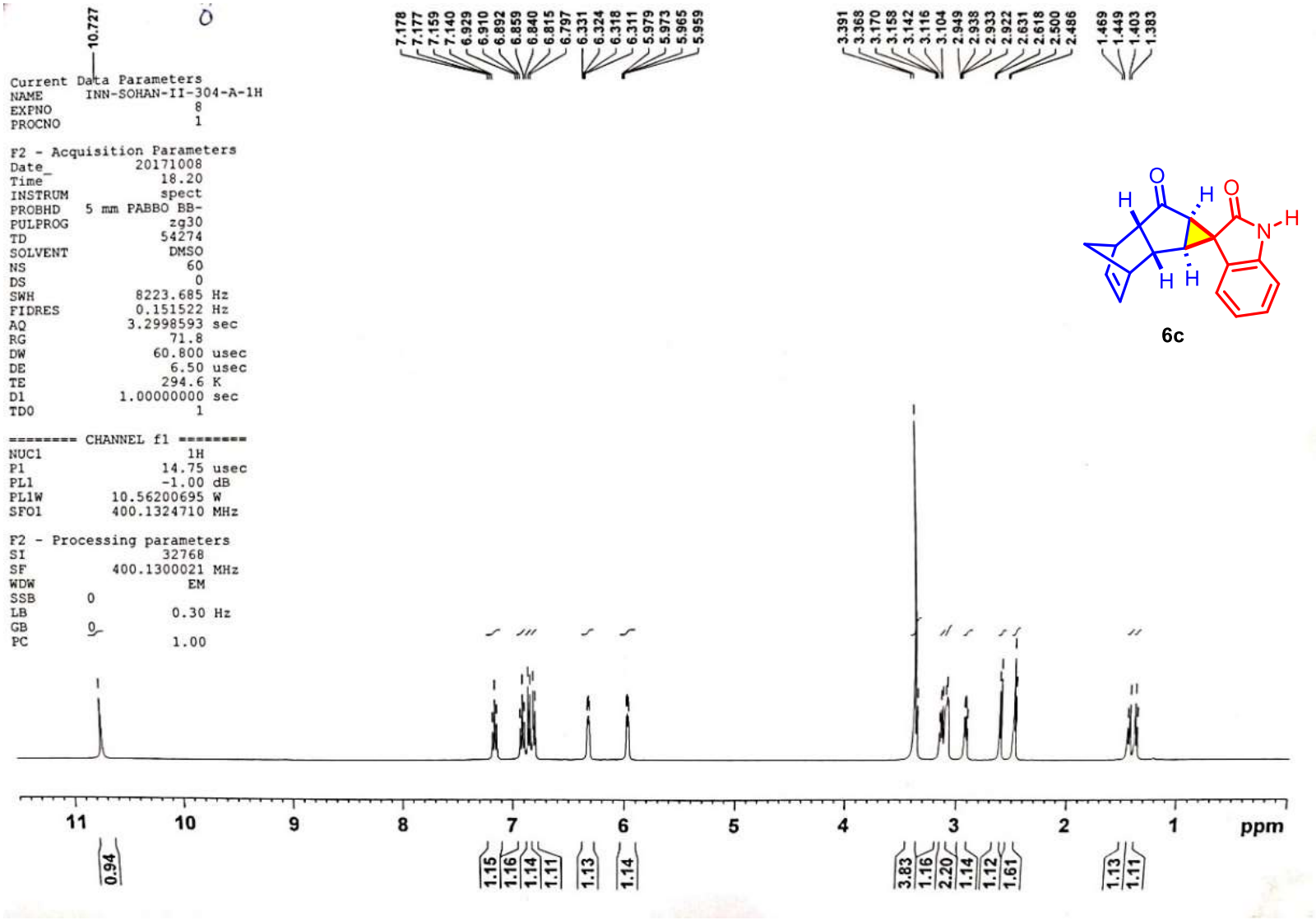


Figure S31. ^{1}H NMR of compound **6c**

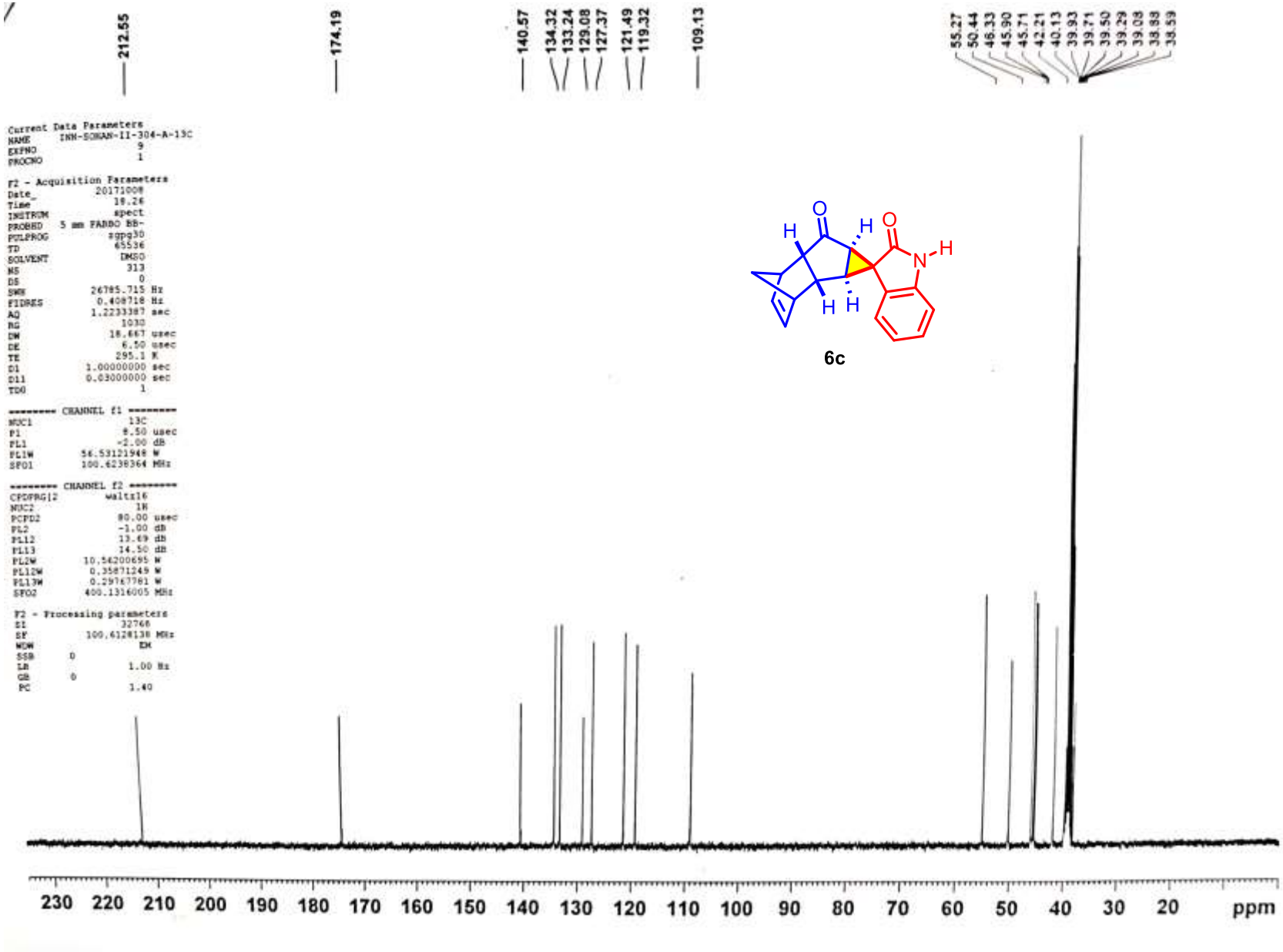


Figure S32. ^{13}C NMR of compound **6c**

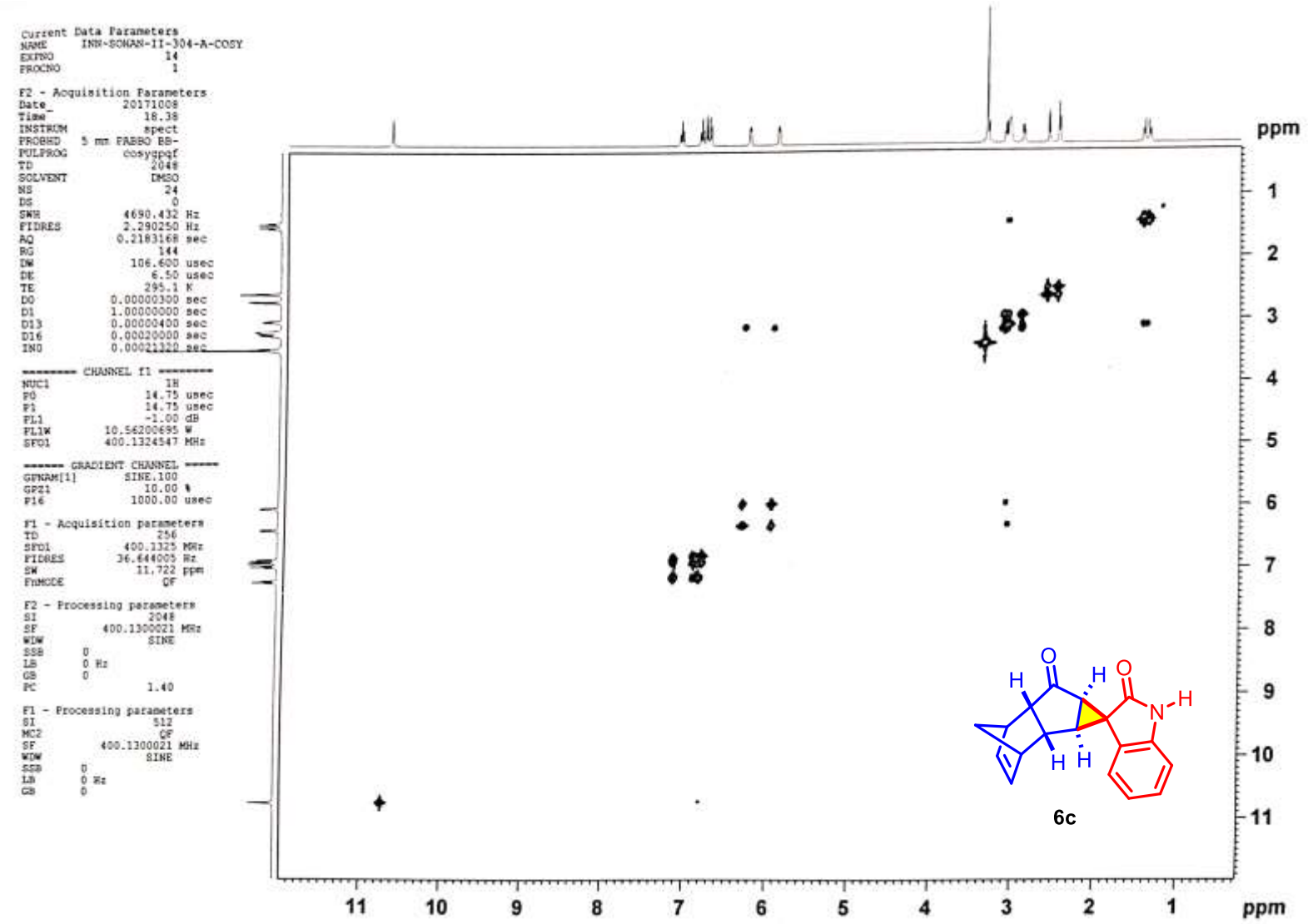


Figure S33. ^{1}H-^{1}H COSY NMR of compound **6c**

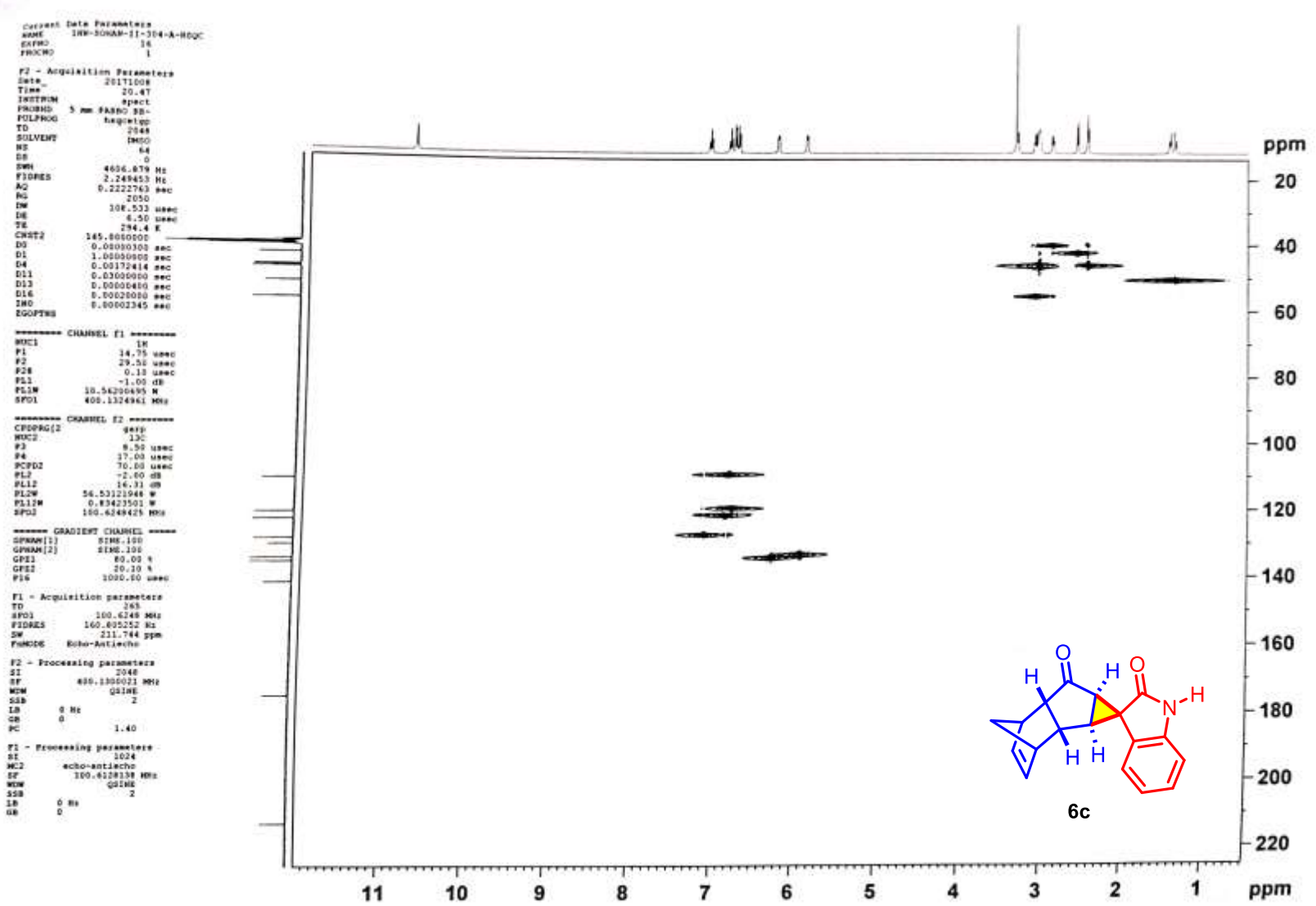


Figure S34. ^{1}H-^{13}C HSQC NMR of compound **6c**

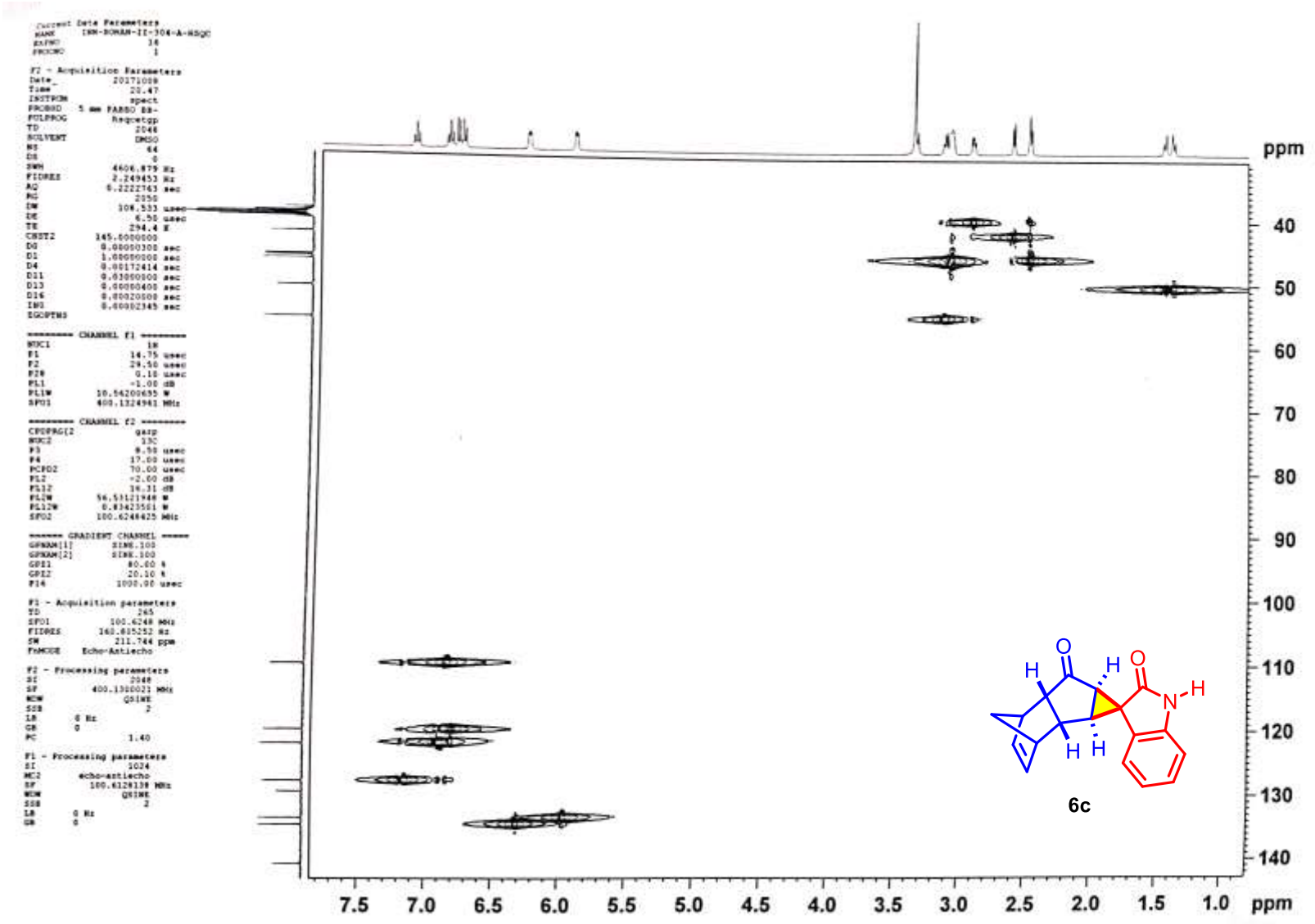


Figure S34a. Expansion of ^{1}H-^{13}C HSQC NMR of compound **6c**

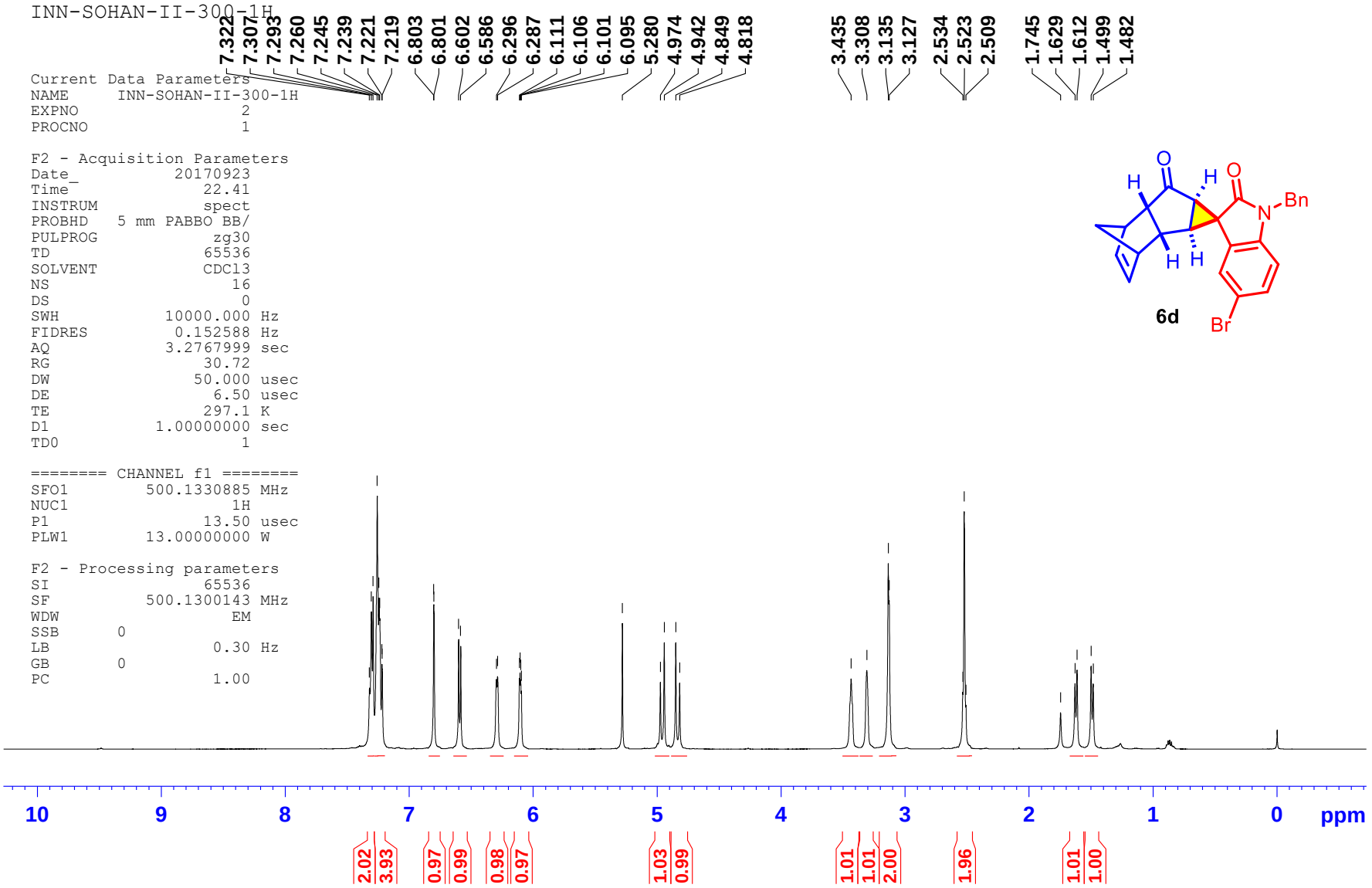


Figure S35. ^{1}H NMR of compound **6d**

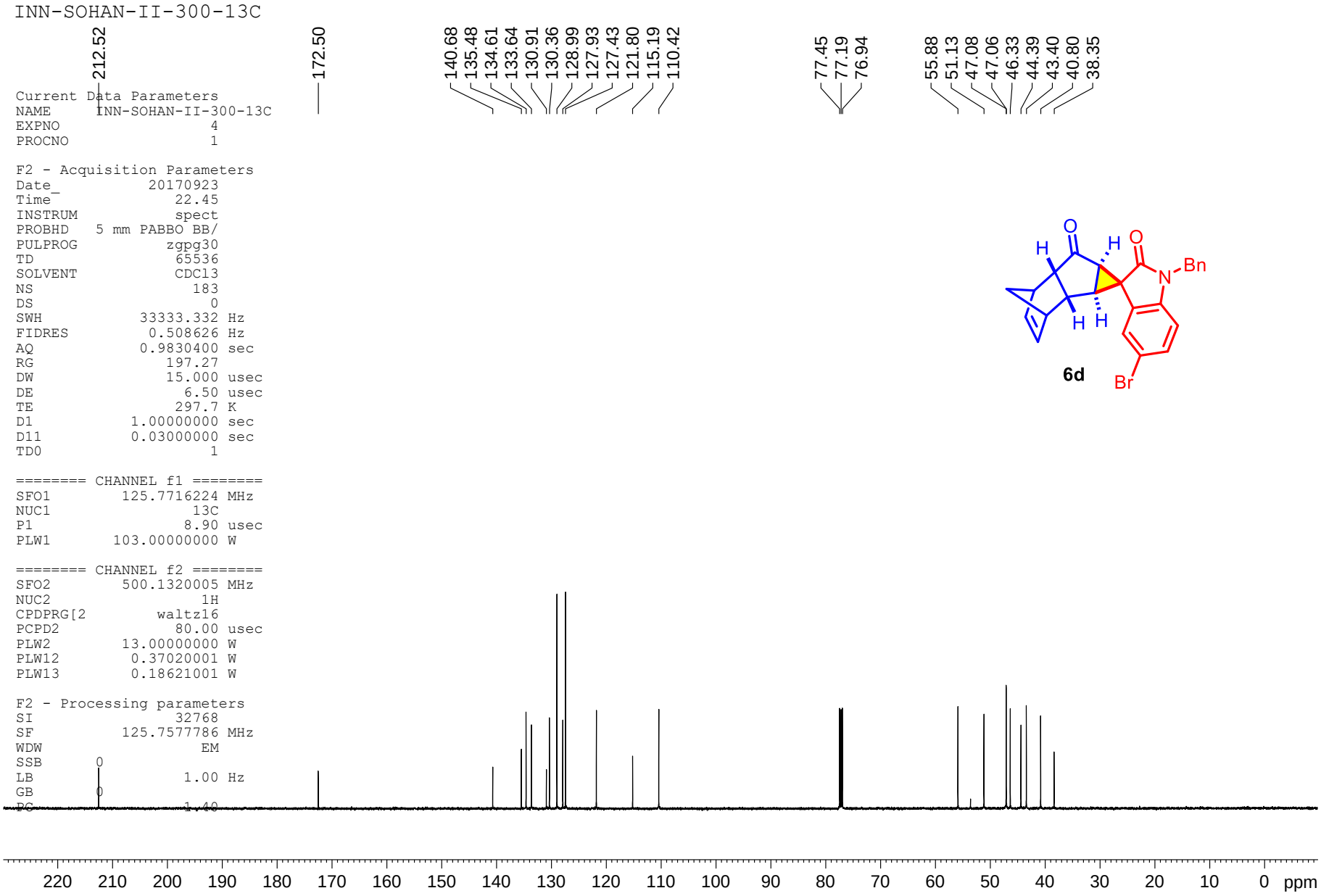


Figure S36. ^{13}C NMR of compound **6d**

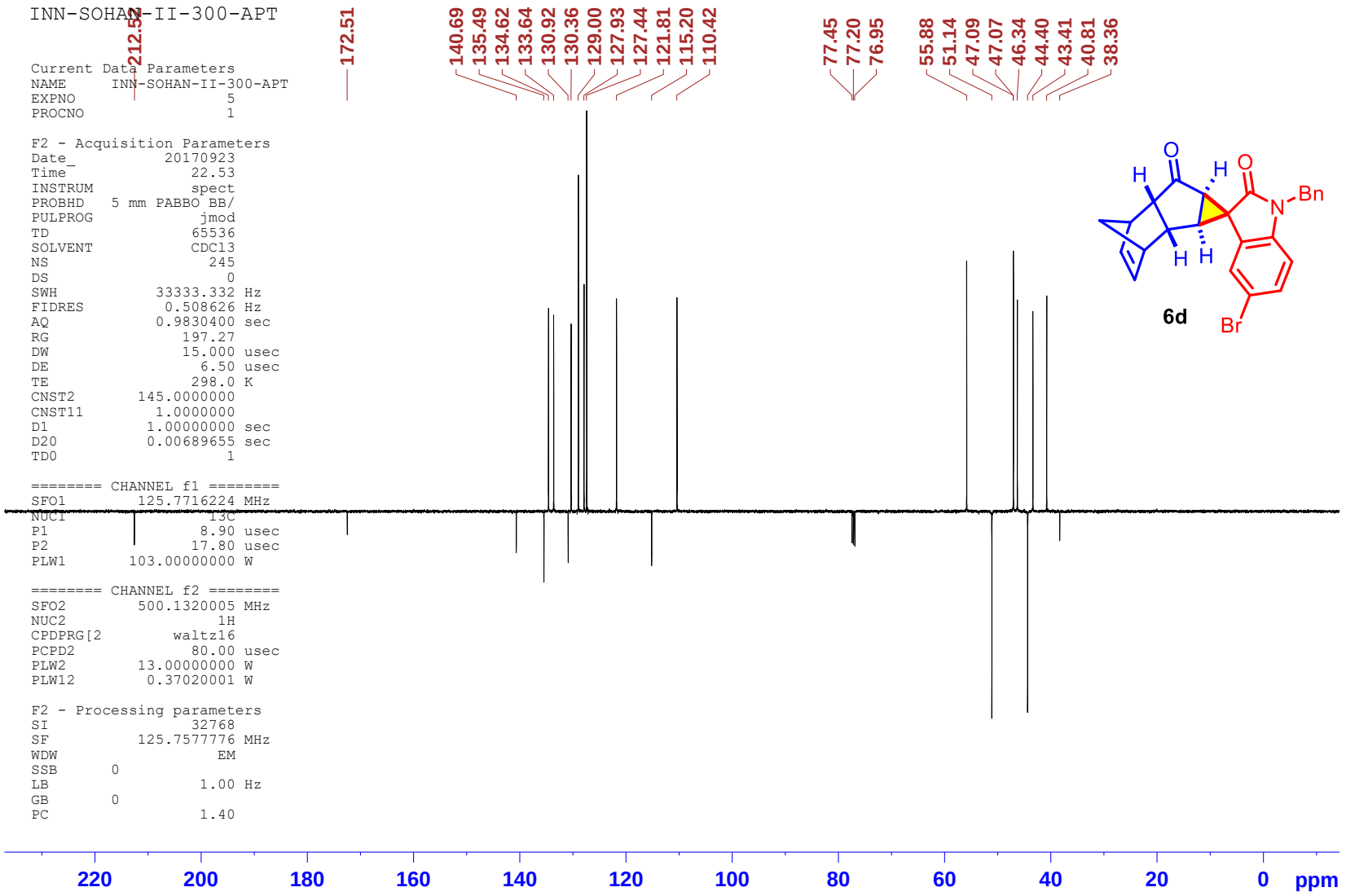


Figure S37. ^{13}C-APT NMR of compound **6d**

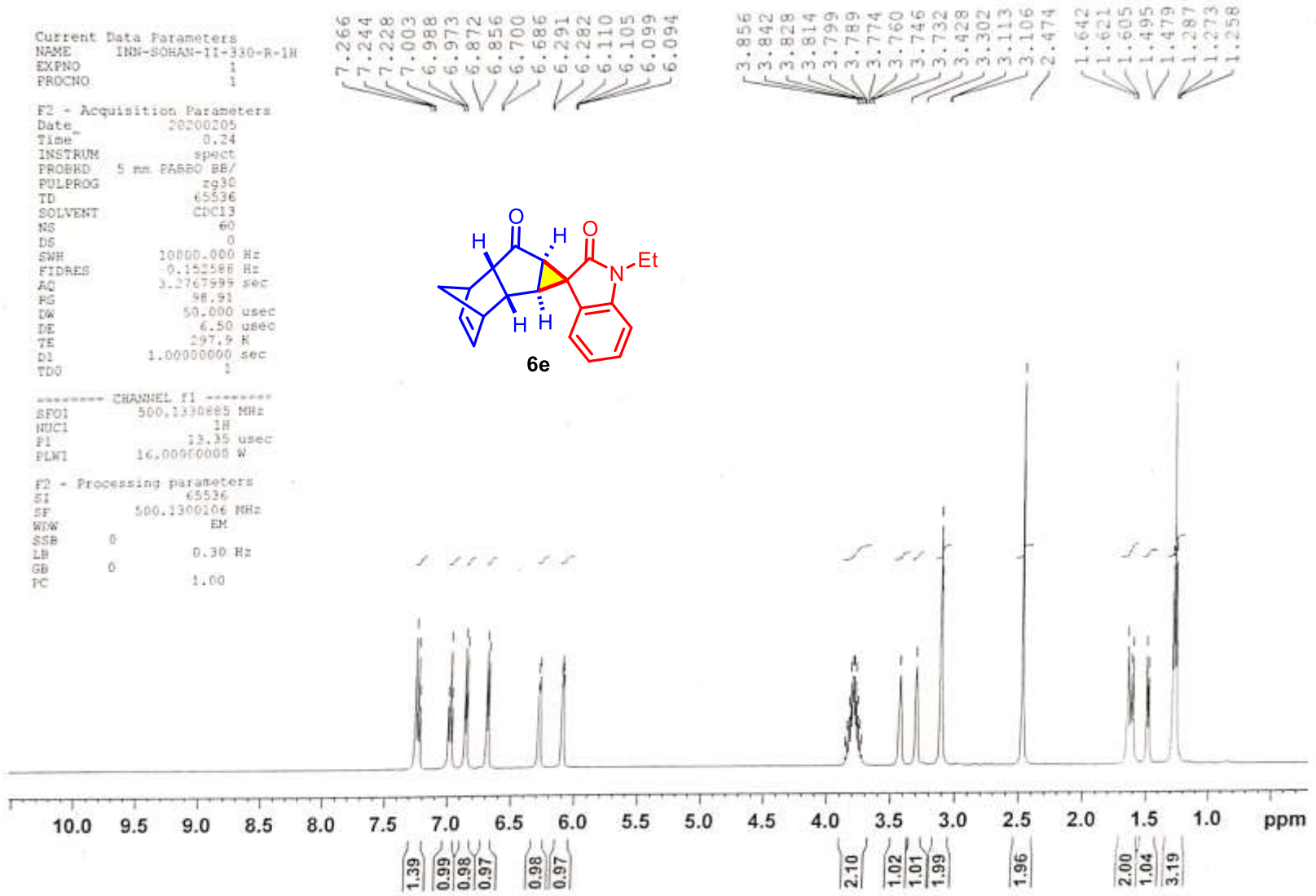


Figure S38. ^{1}H NMR of compound **6e**

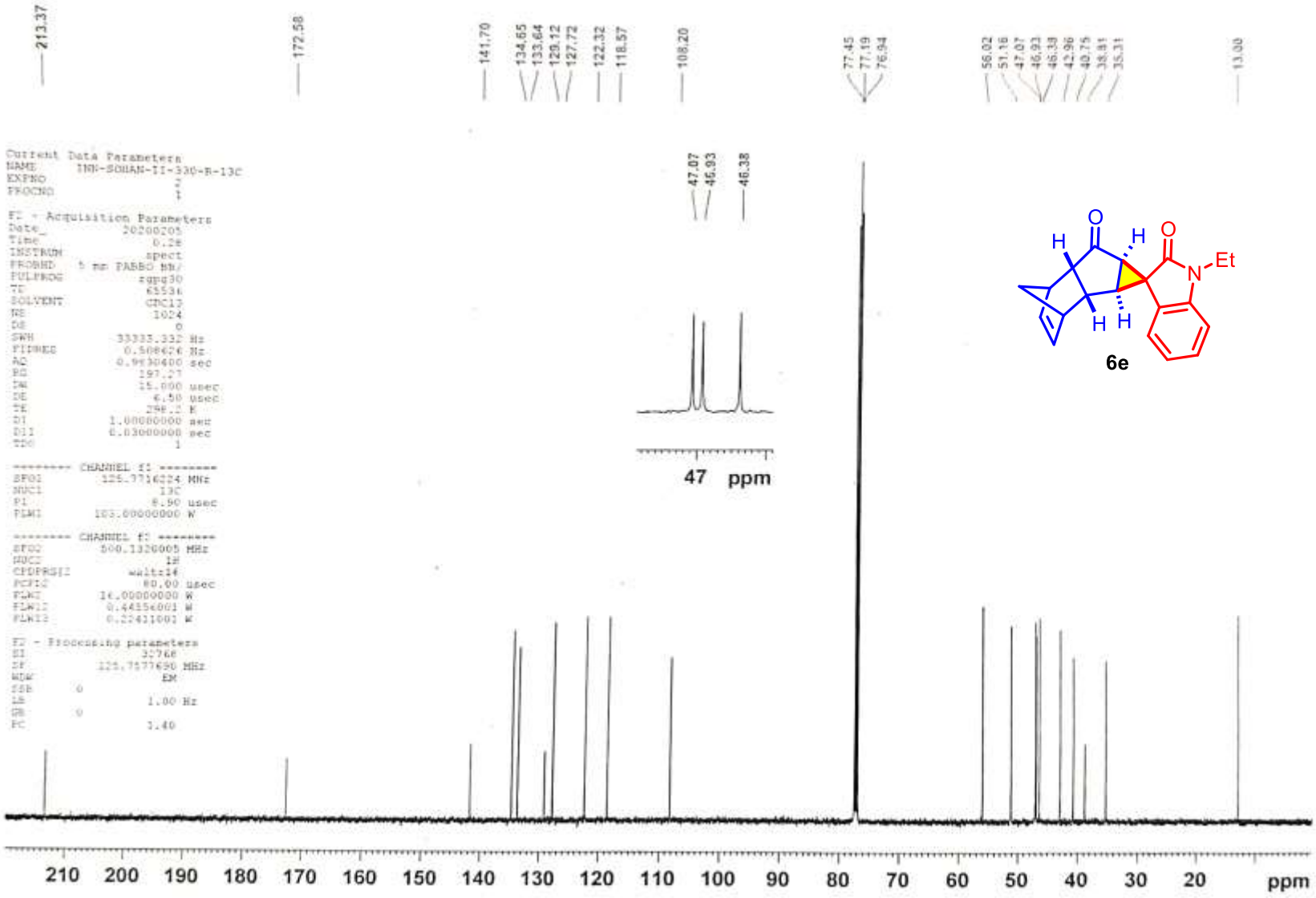


Figure S39. ^{13}C NMR of compound **6e**

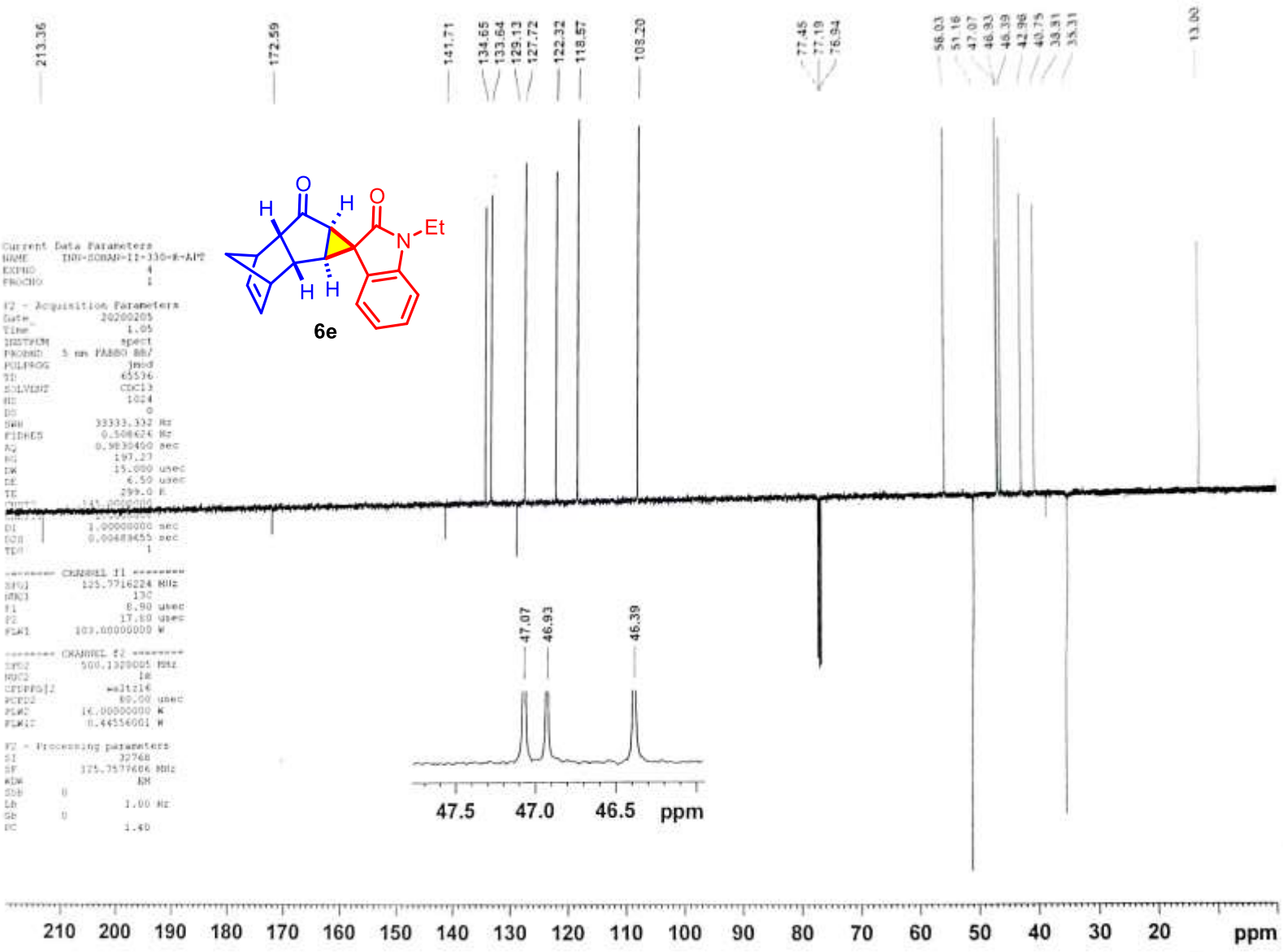


Figure S40. ^{13}C-APT NMR of compound **6e**

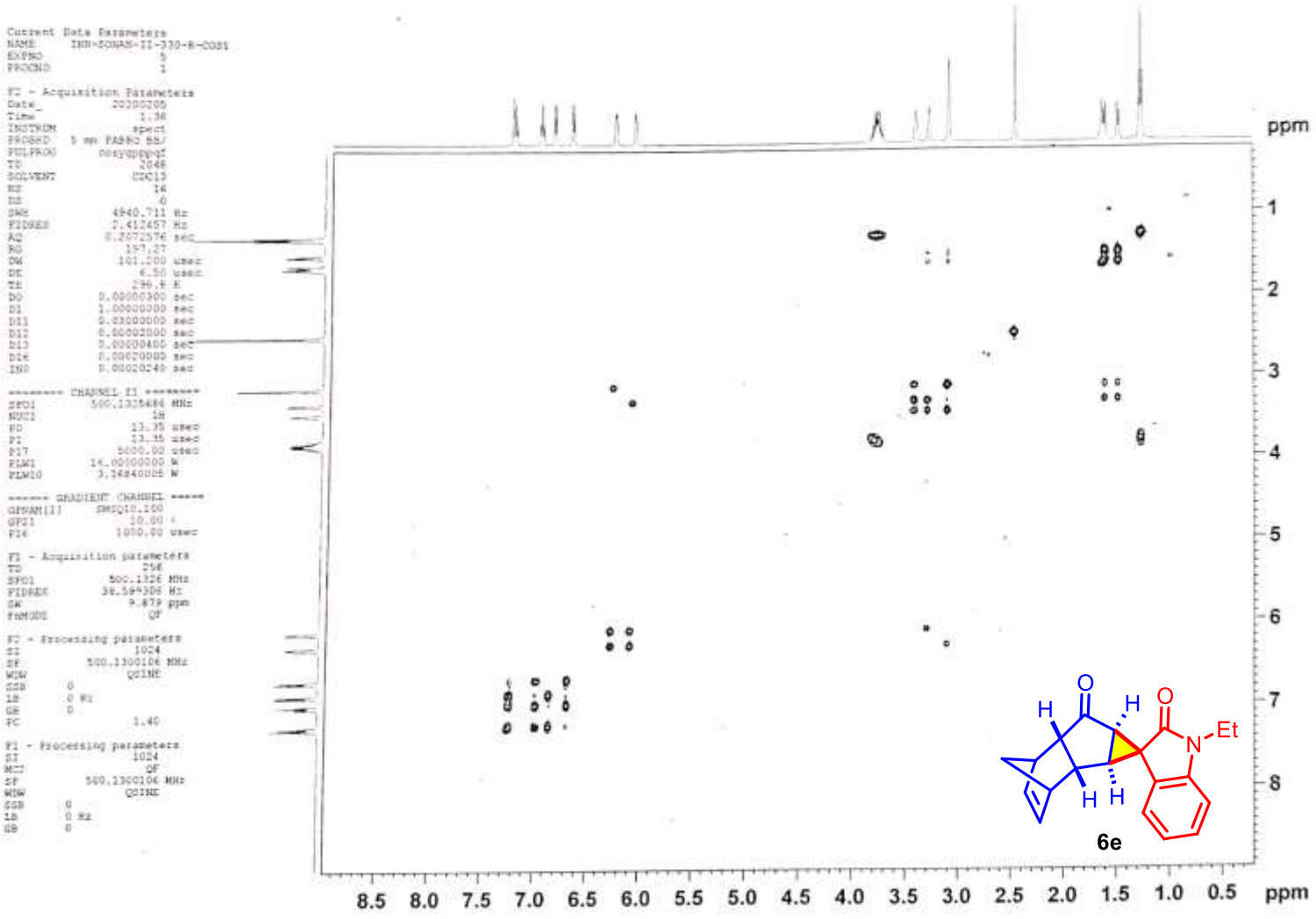


Figure S41. ^{1}H-^{1}H COSY NMR of compound **6e**

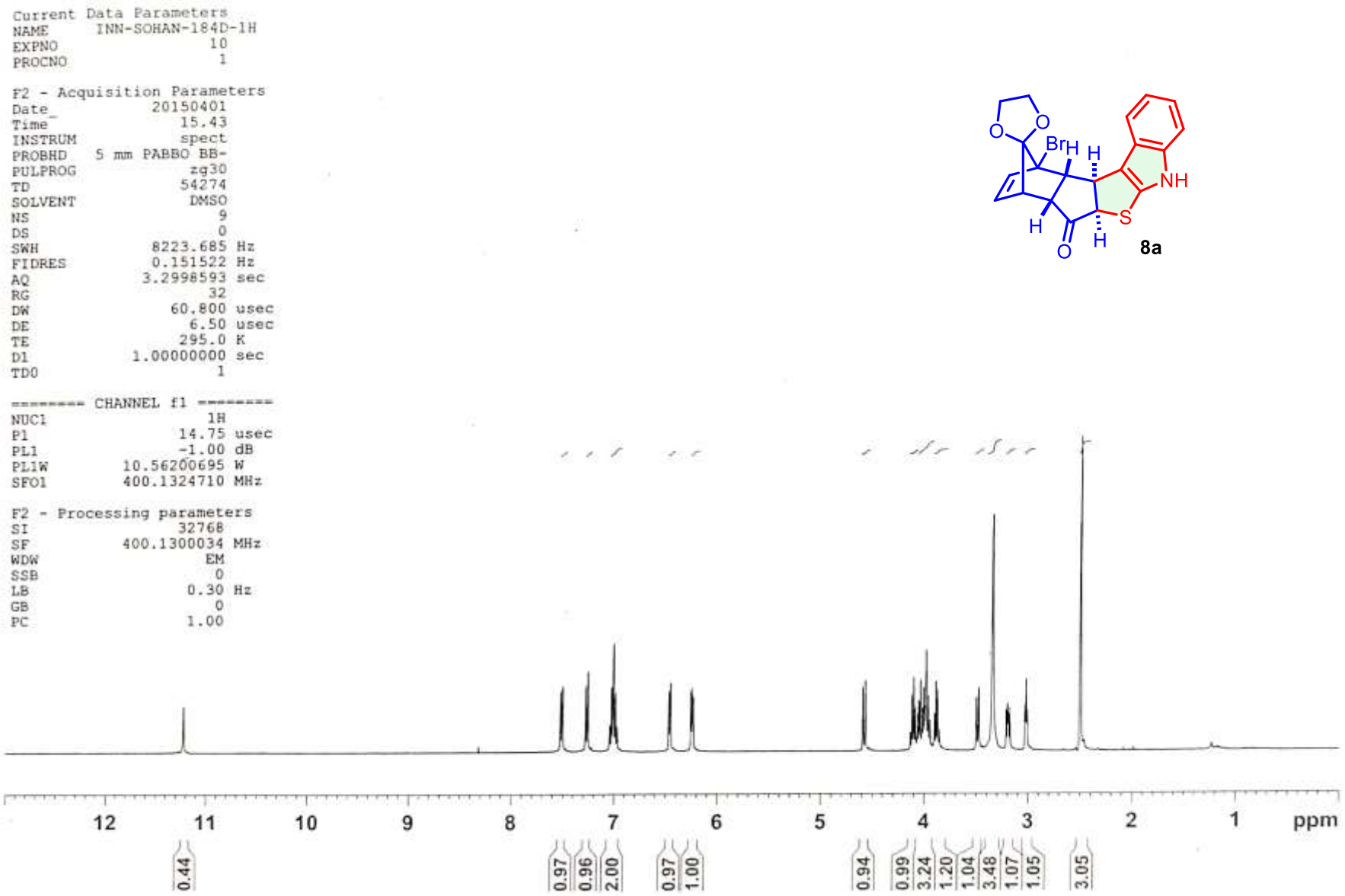


Figure S42. ^{1}H NMR of compound **8a**

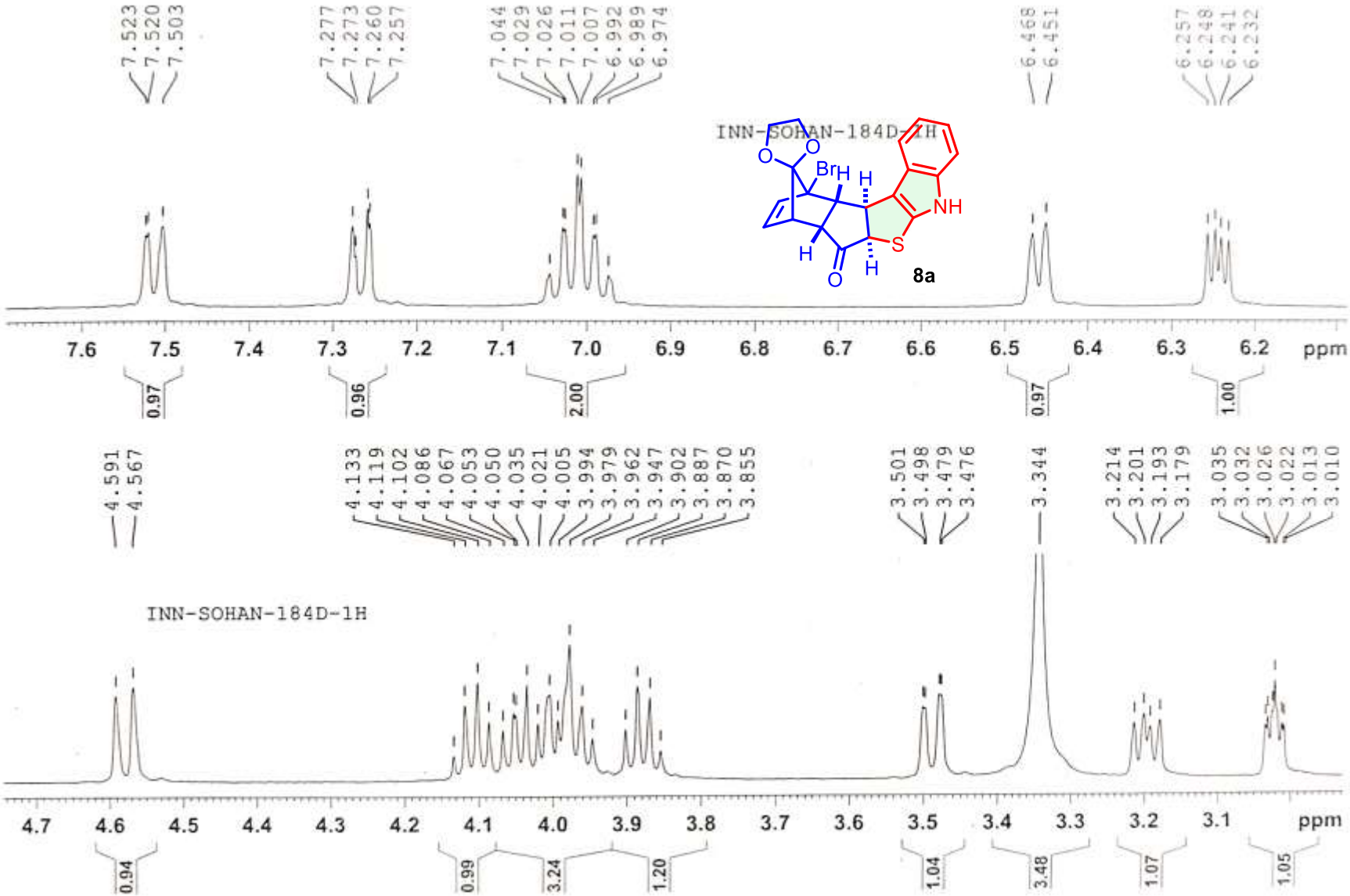


Figure S42a. Expansion of ^{1}H NMR of compound **8a**

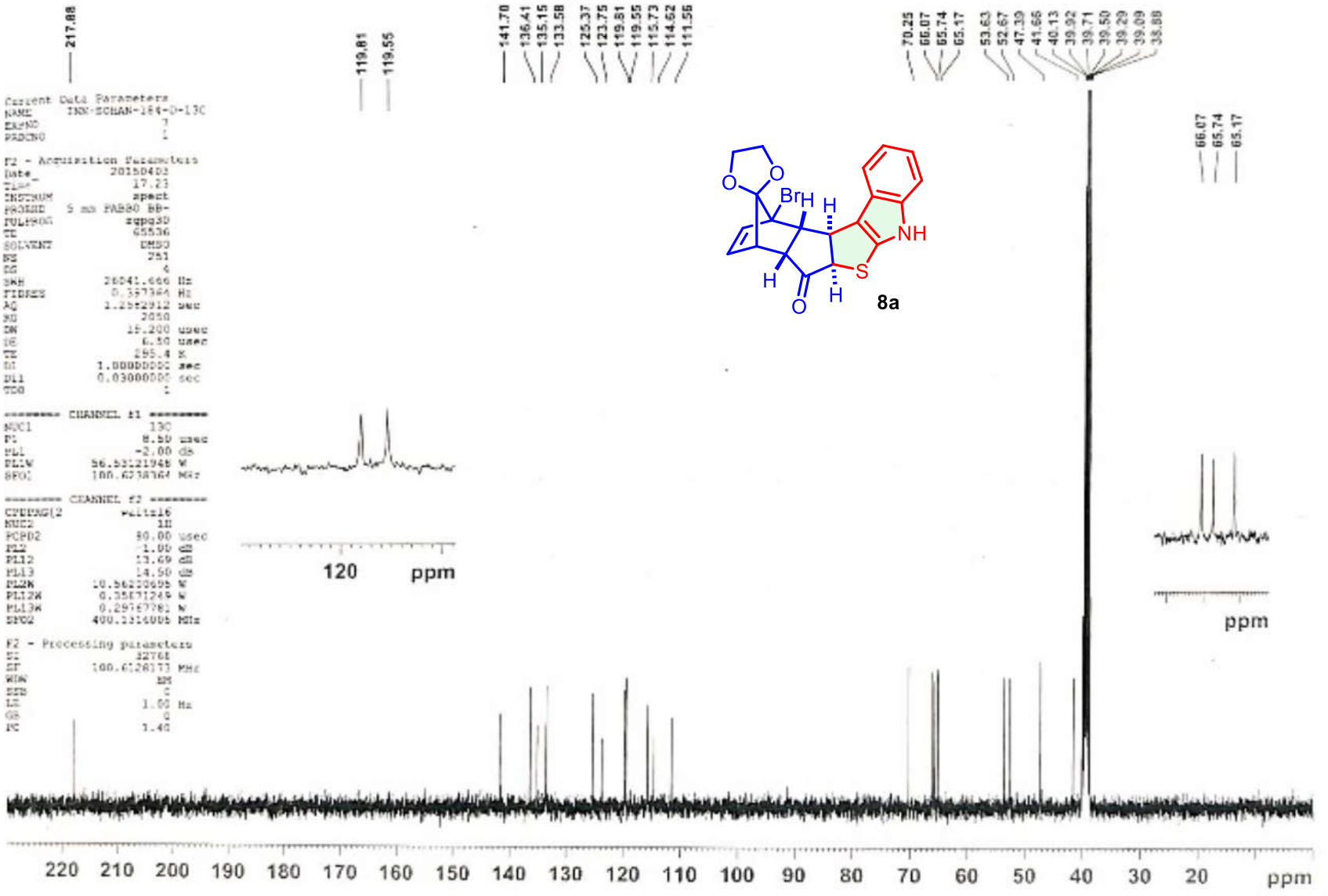


Figure S43. ^{13}C NMR of compound **8a**

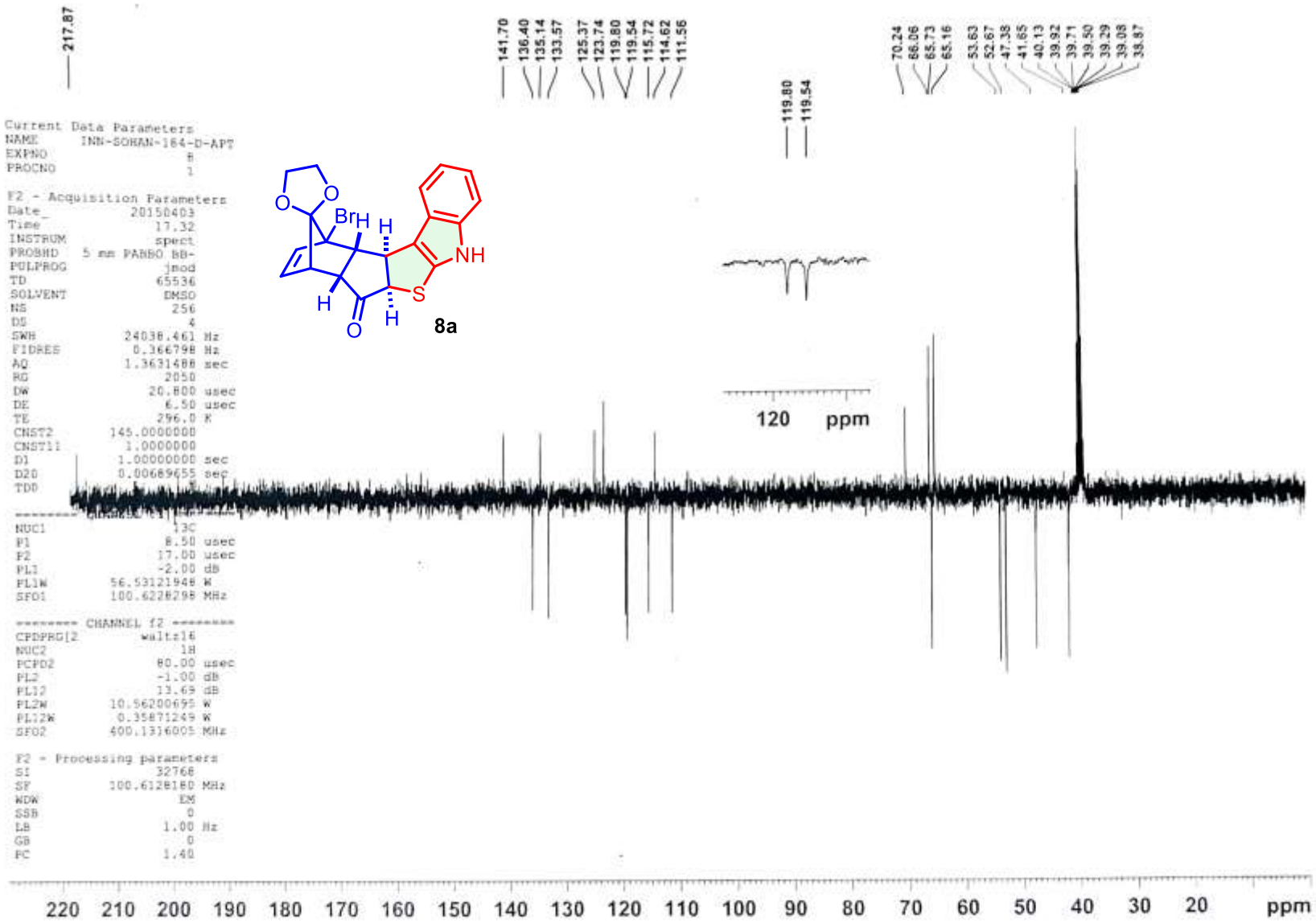


Figure S44. ^{13}C-APT NMR of compound **8a**

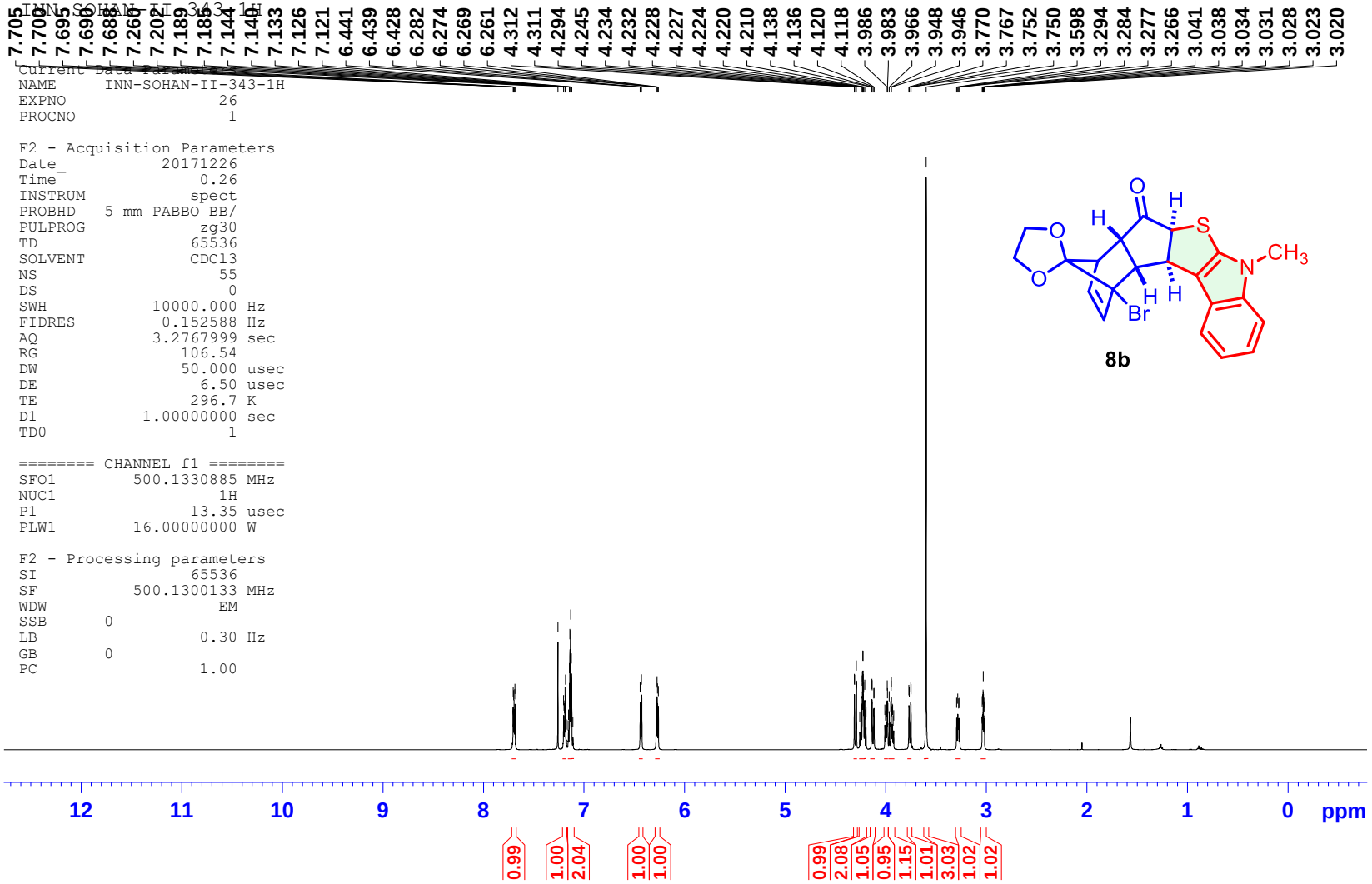


Figure S45. ^{1}H NMR of compound **8b**

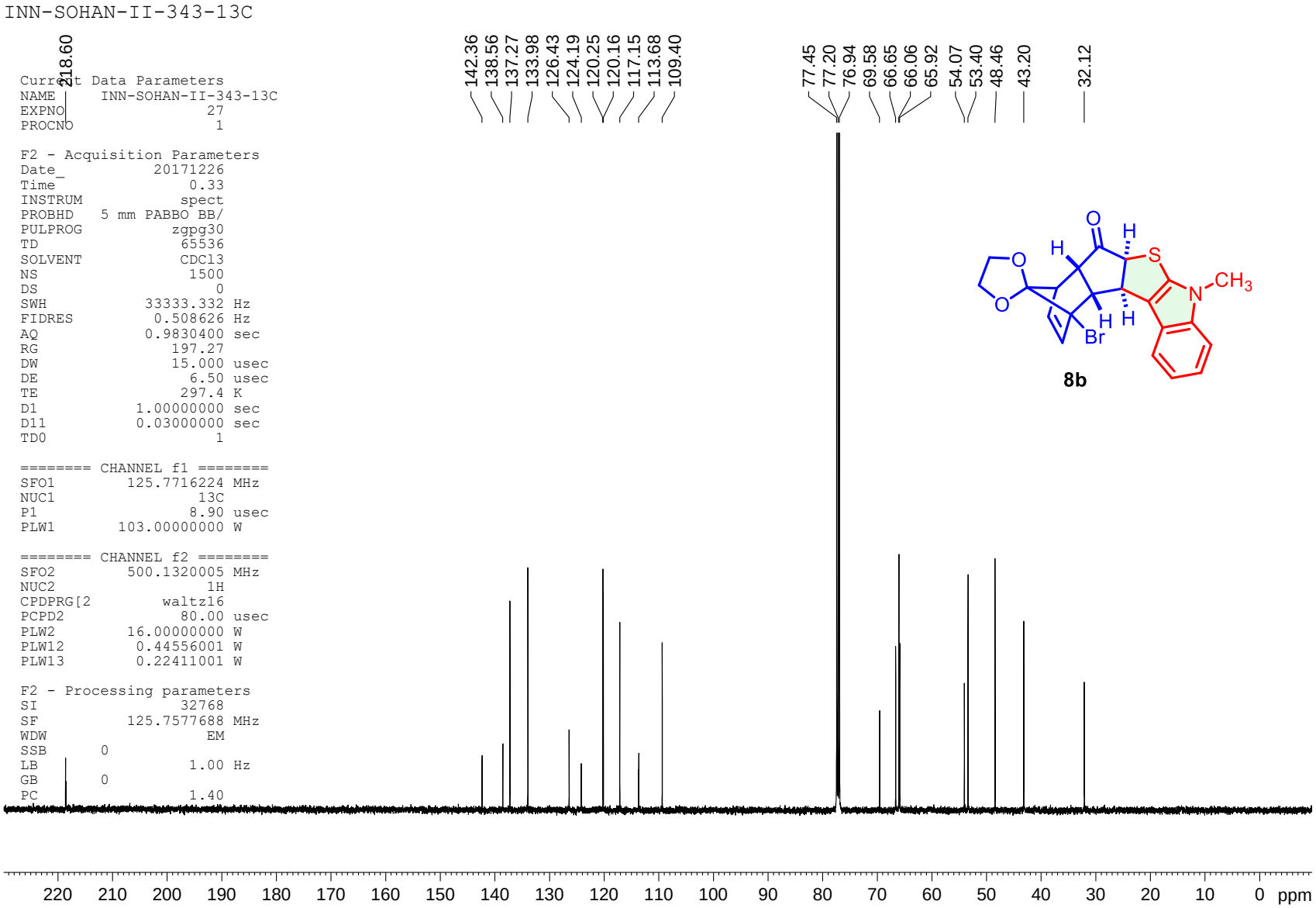


Figure S46. ^{13}C NMR of compound **8b**

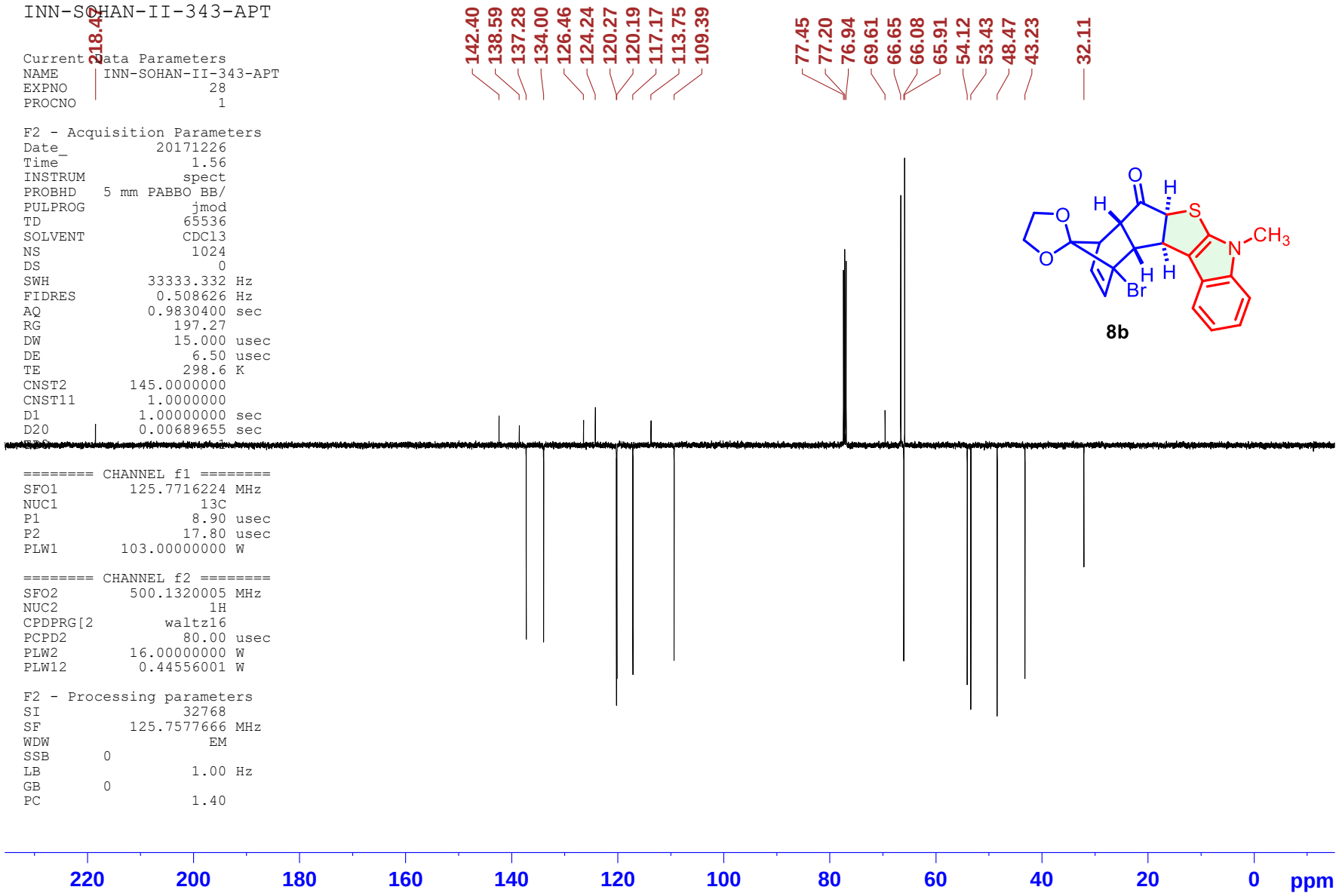


Figure S47. ^{13}C-APT NMR of compound **8b**

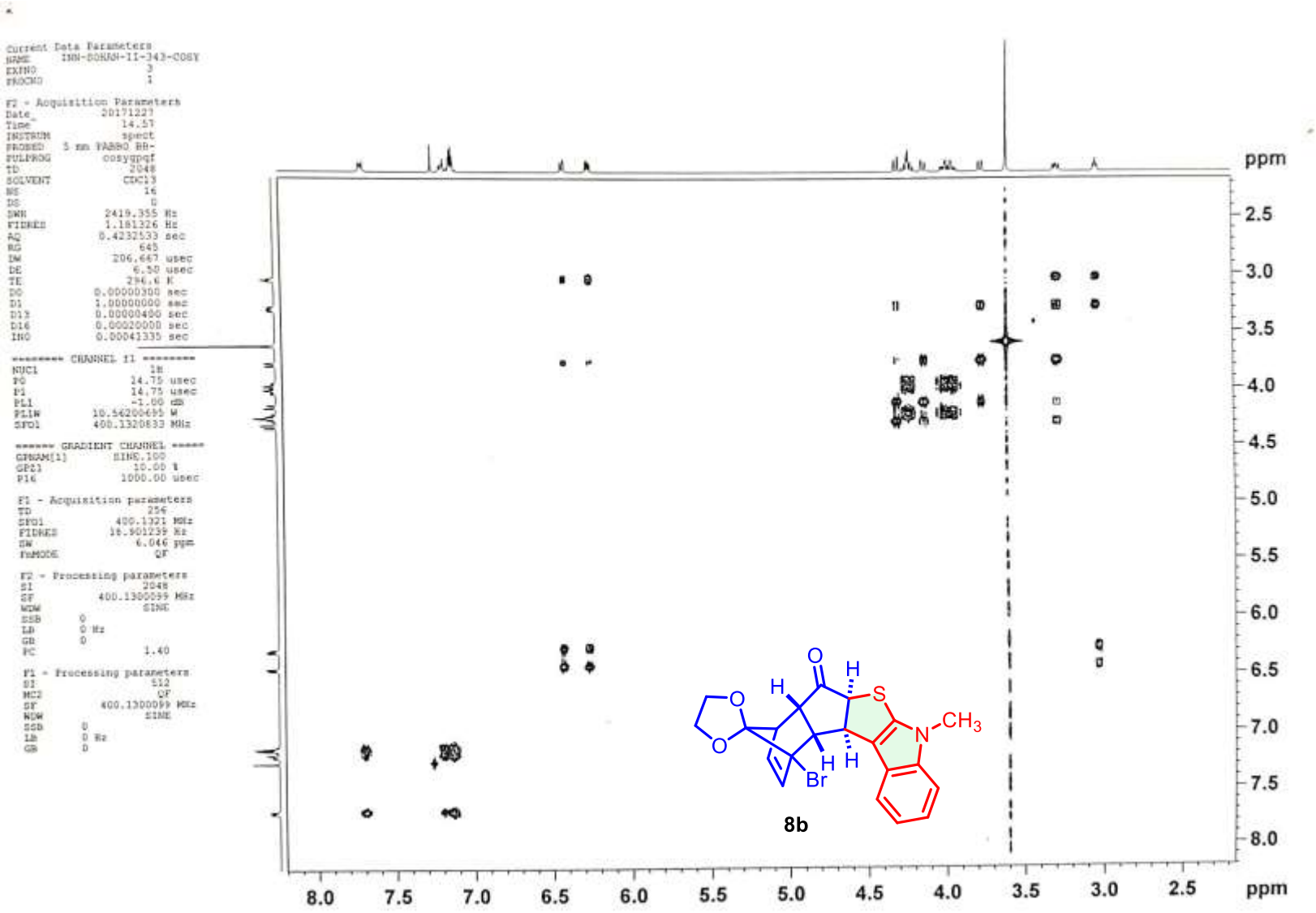


Figure S48. ^{1}H-^{1}H COSY NMR of compound **8b**

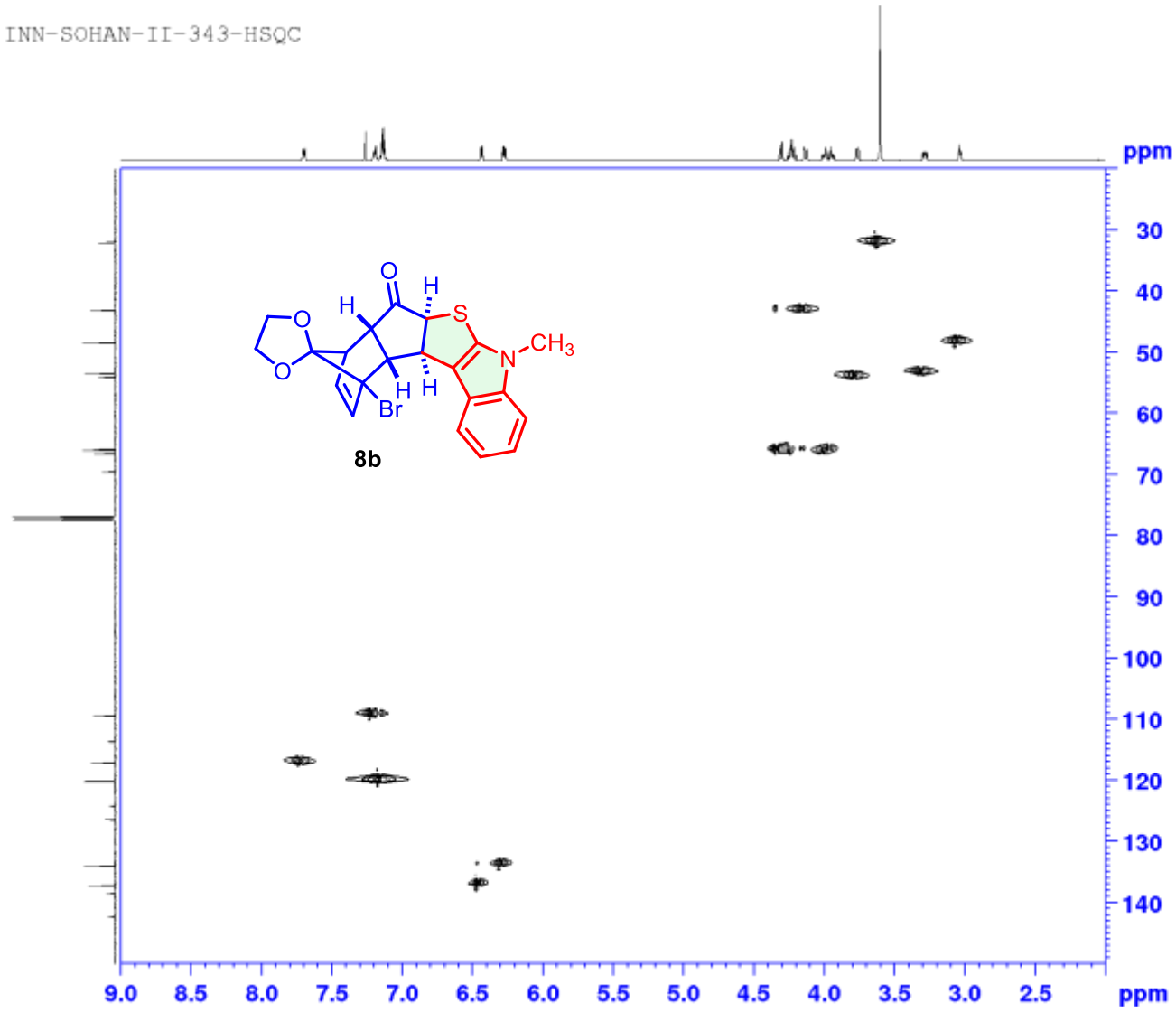


Figure S49. ^{1}H-^{13}C HSQC NMR of compound **8b**

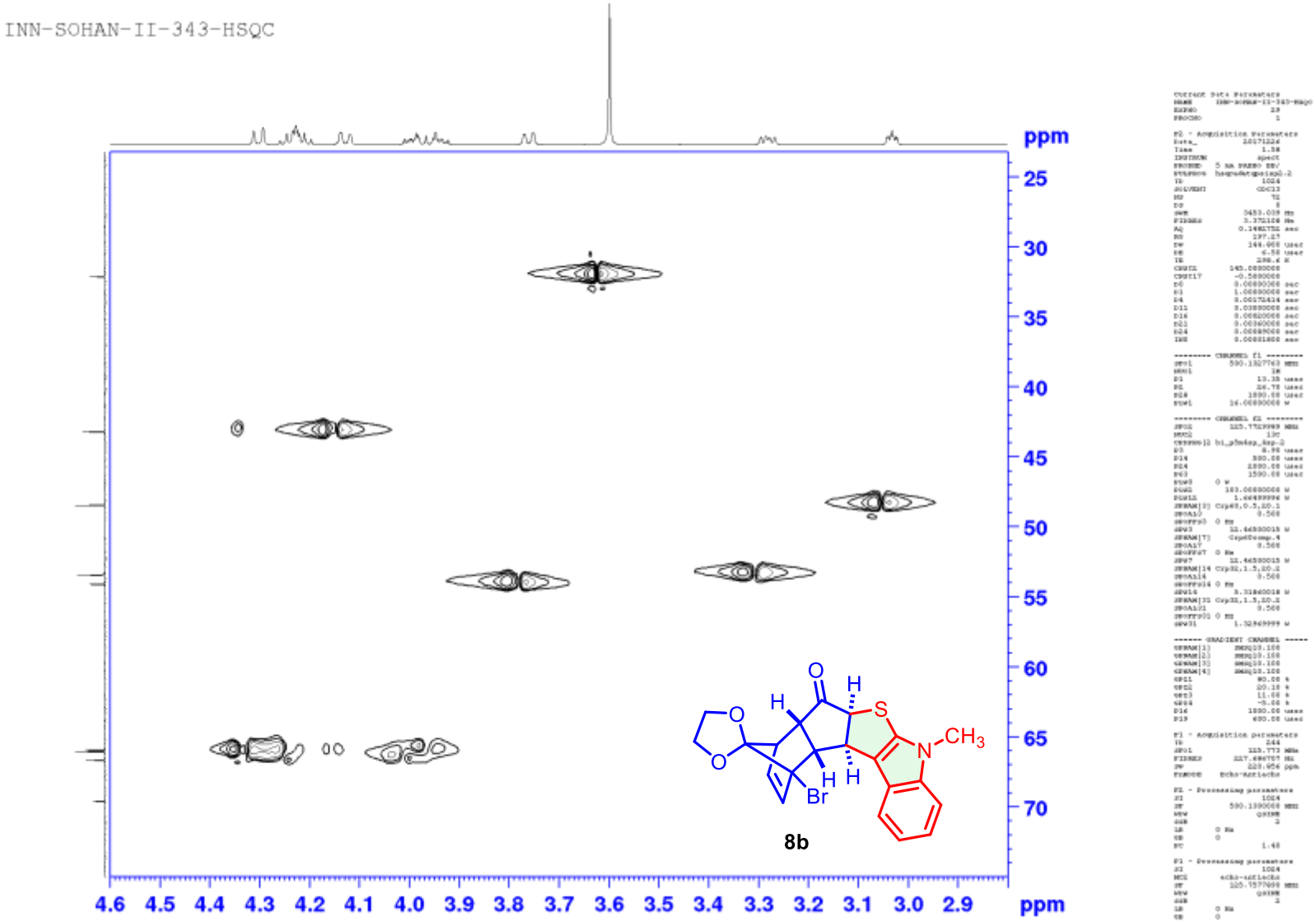
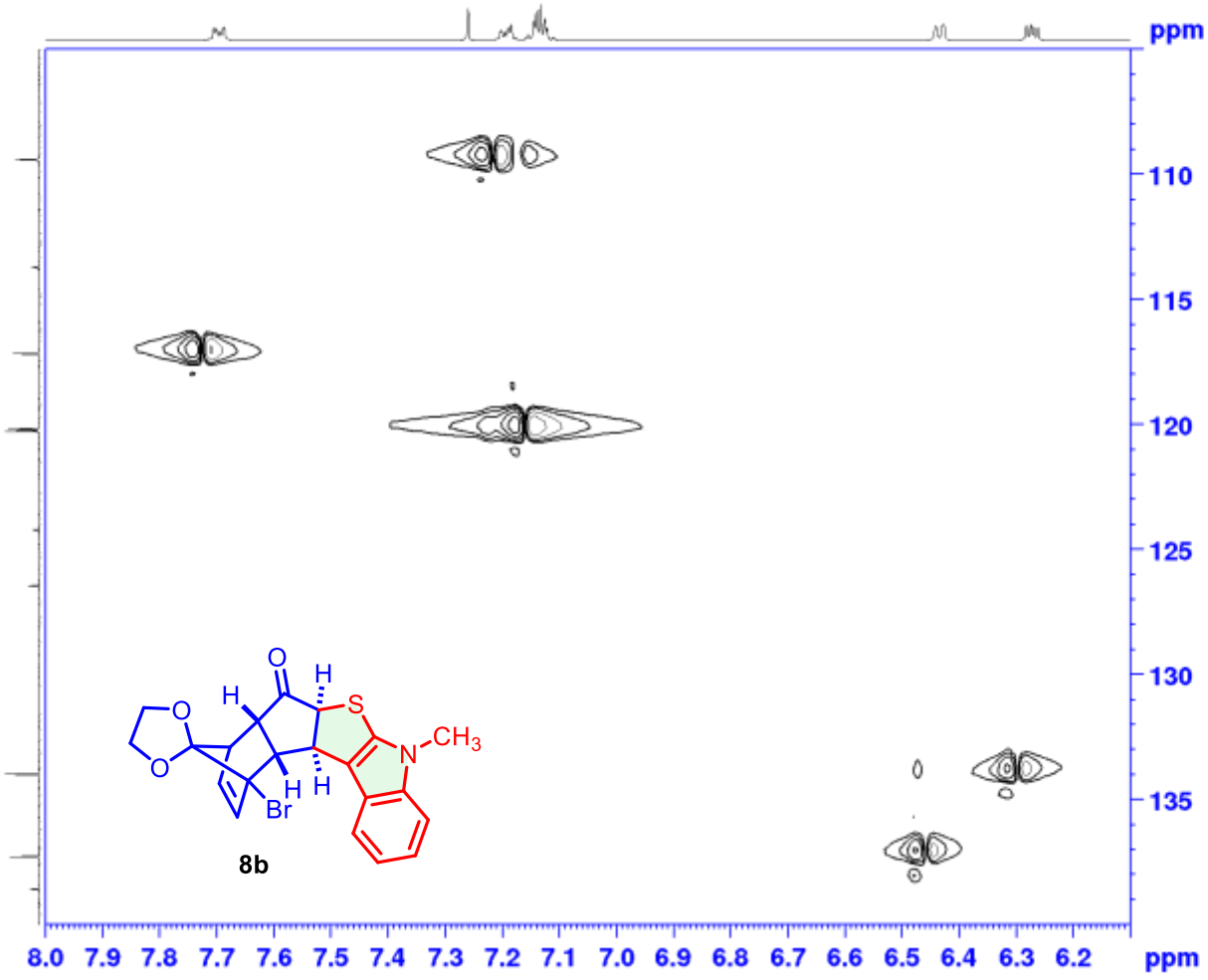


Figure S49a. Expansion of ^{1}H-^{13}C HSQC of compound **8b**



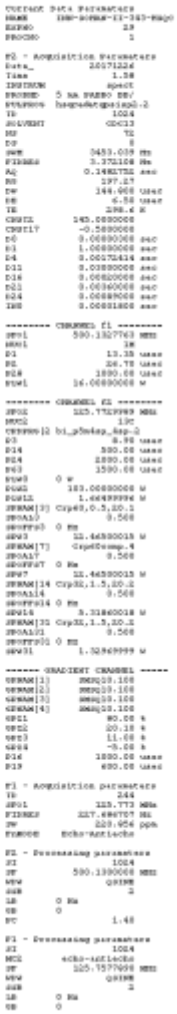


Figure S49b. Expansion of ^{1}H-^{13}C HSQC of compound **8b**

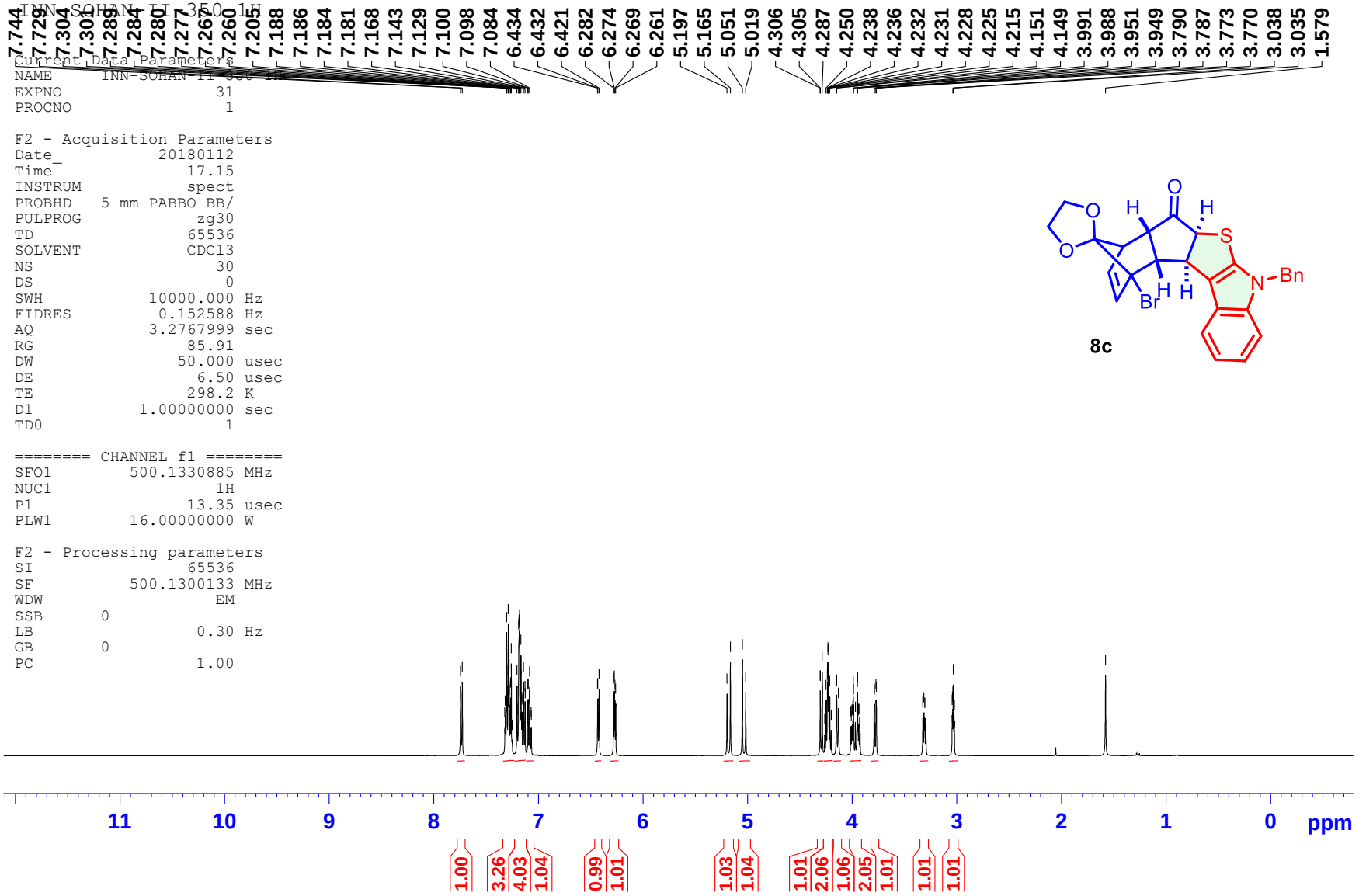


Figure S50. ^{1}H NMR of compound **8c**

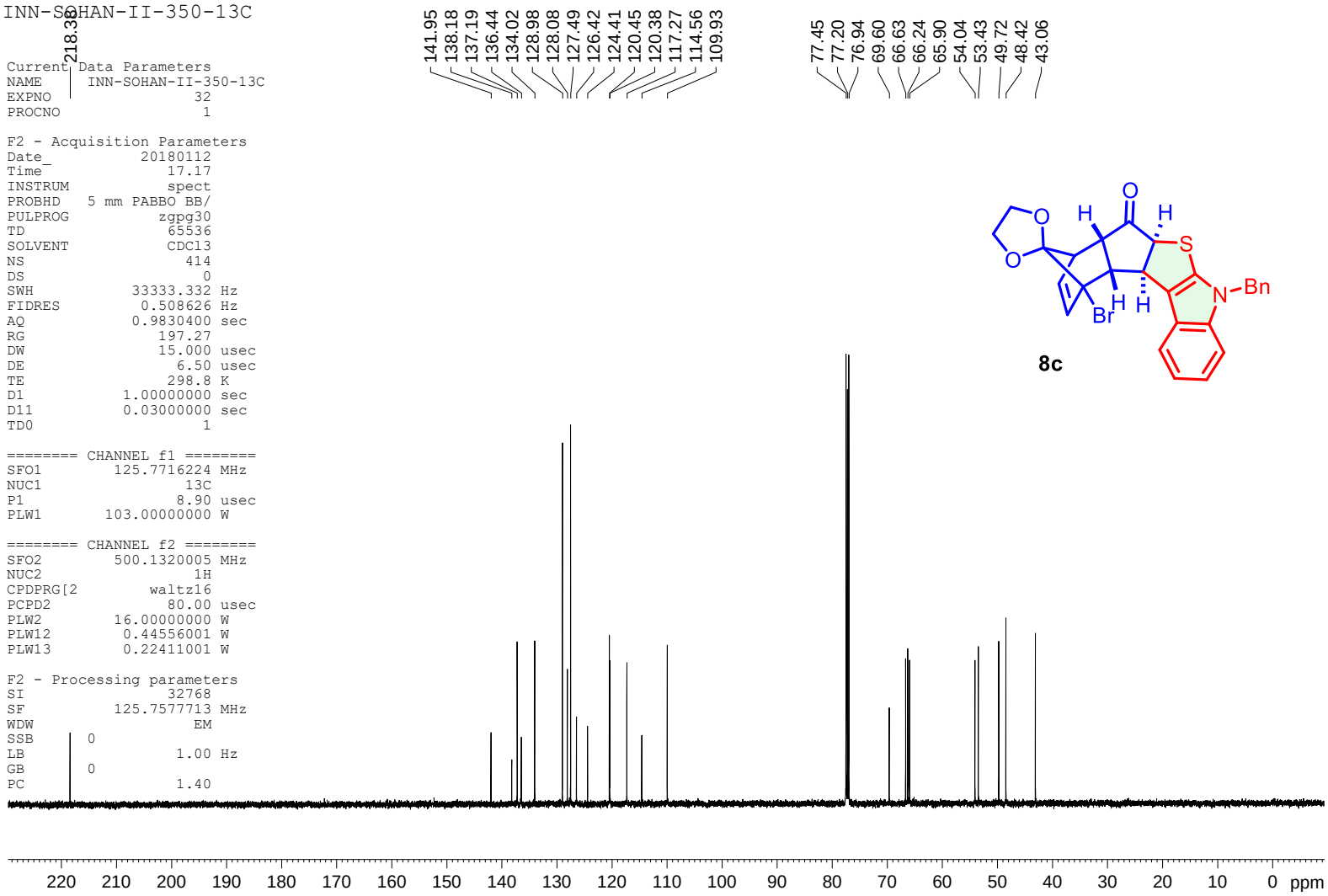


Figure S51. ^{13}C NMR of compound **8c**

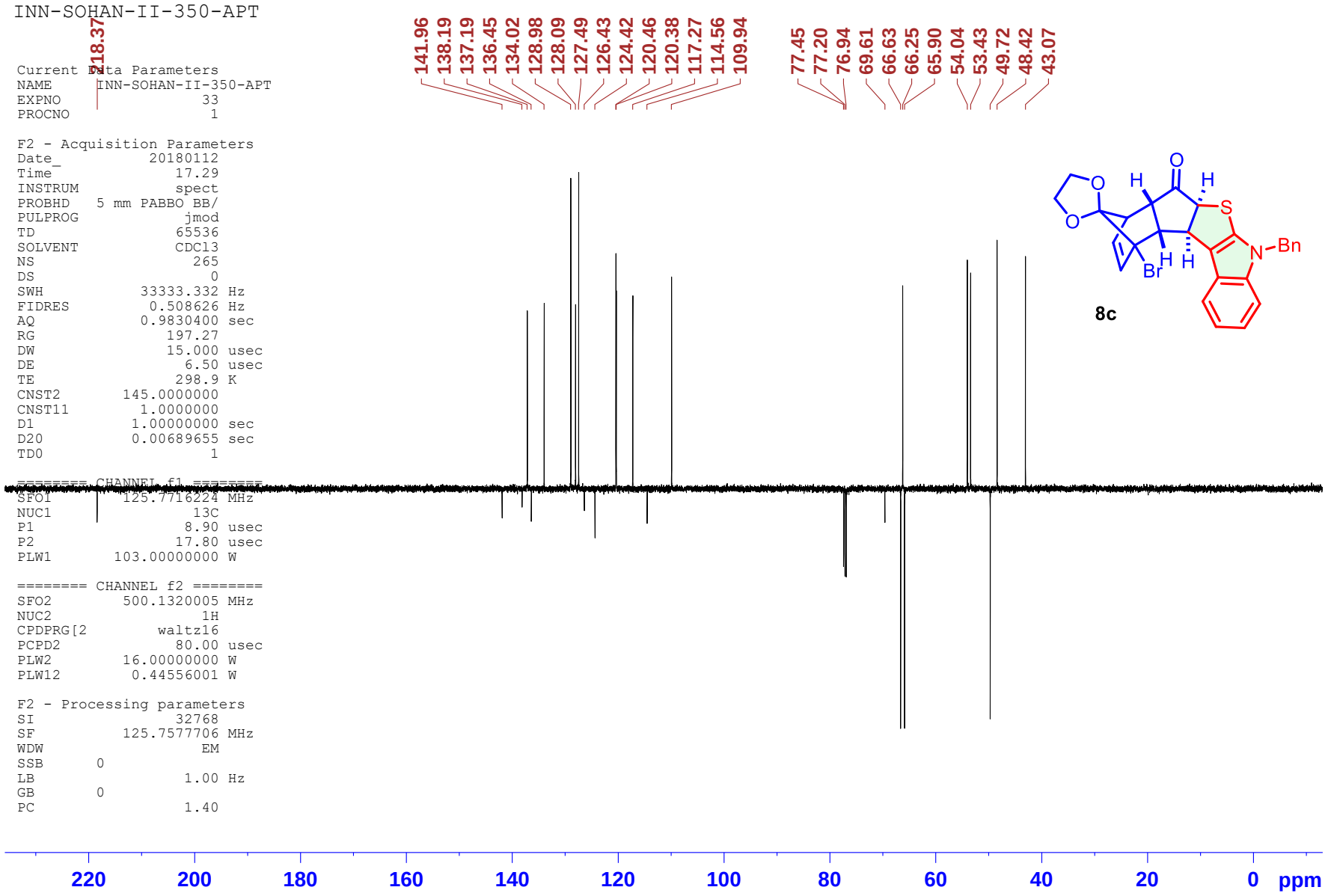


Figure S52. ^{13}C-APT NMR of compound **8c**

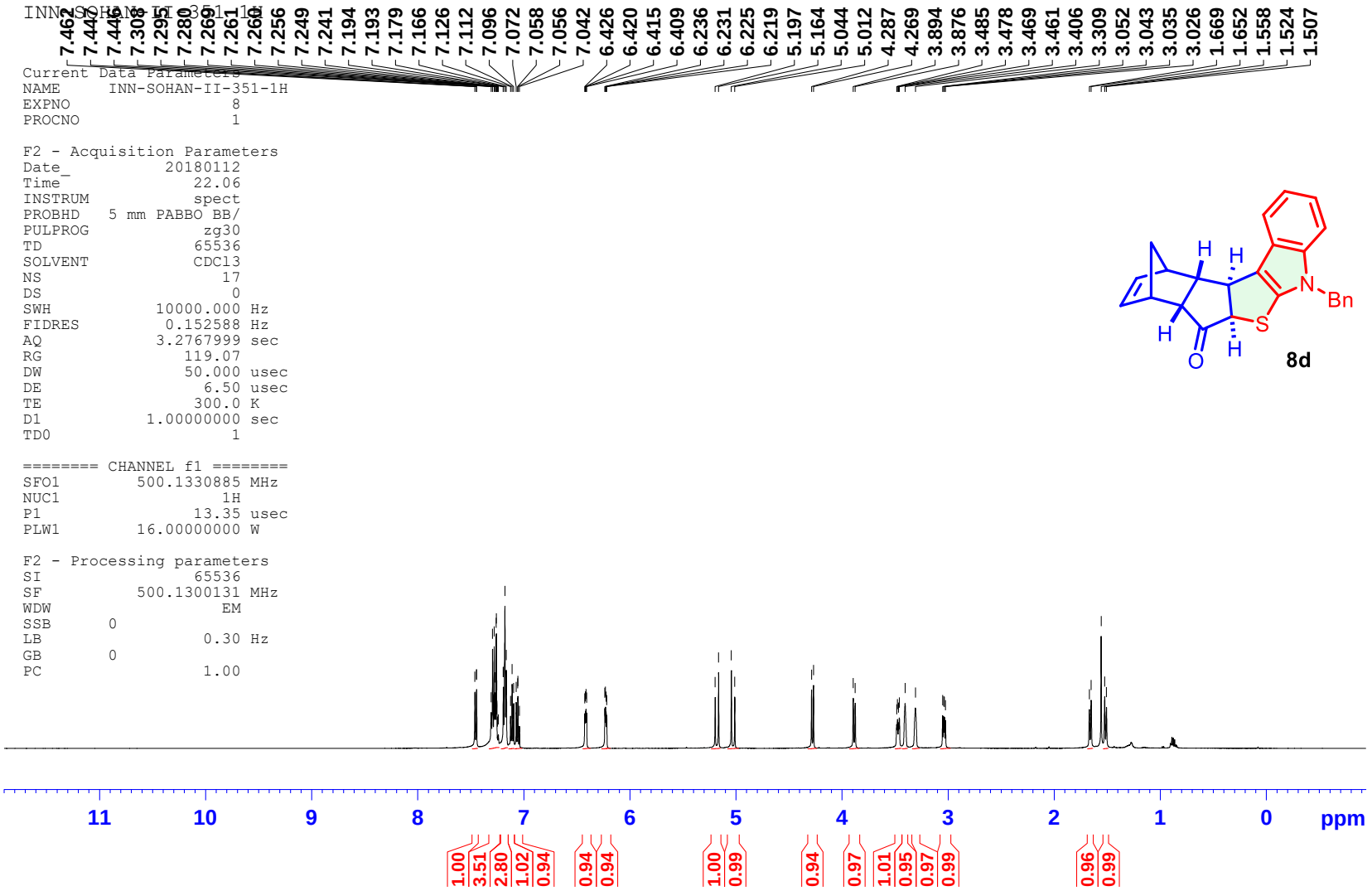


Figure S53. ^{1}H NMR of compound **8d**

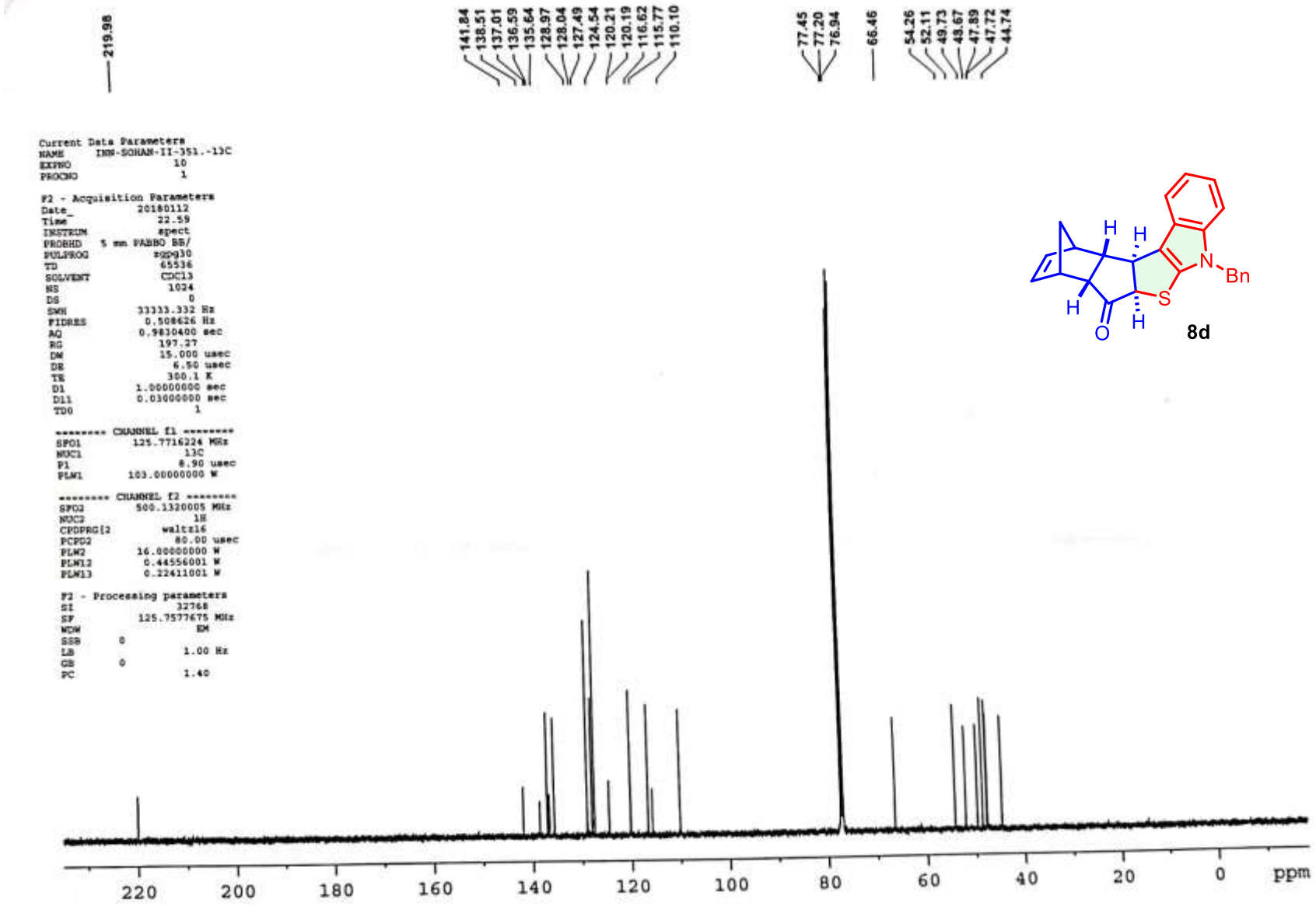


Figure S54. ^{13}C NMR of compound **8d**

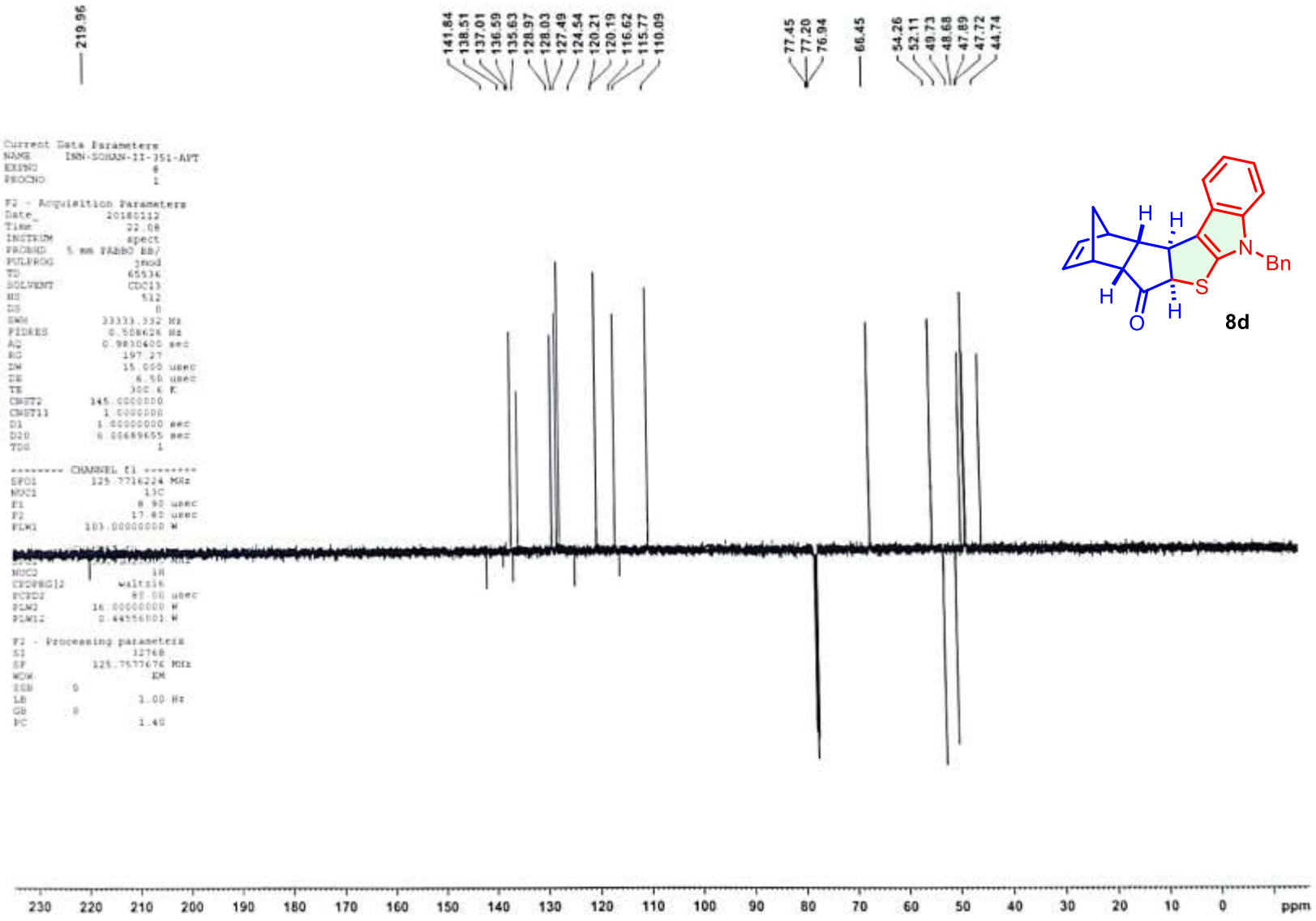


Figure S55. ^{13}C-APT NMR of compound **8d**

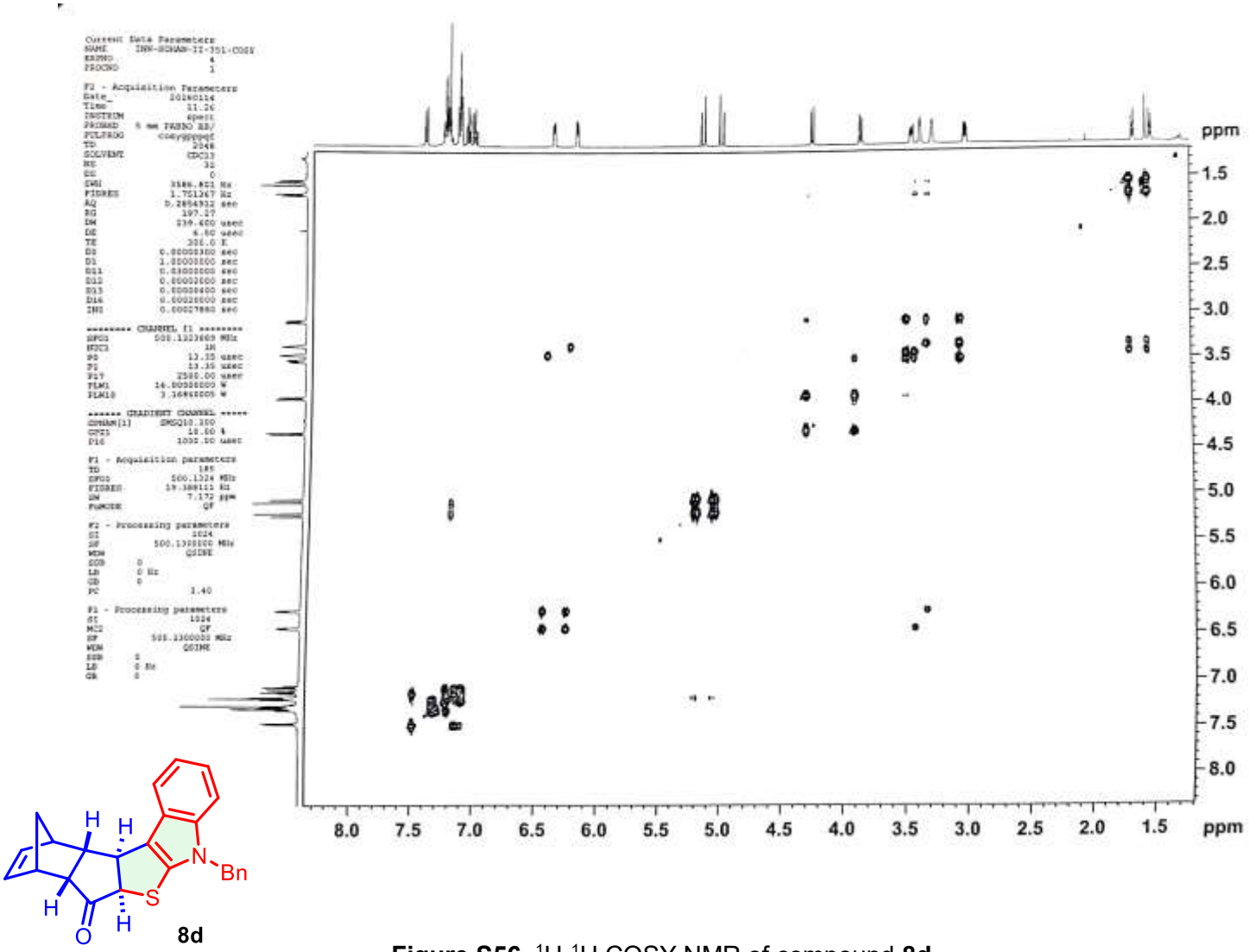
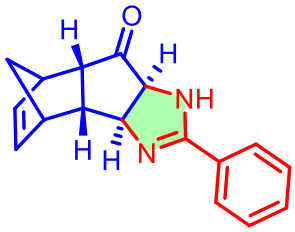
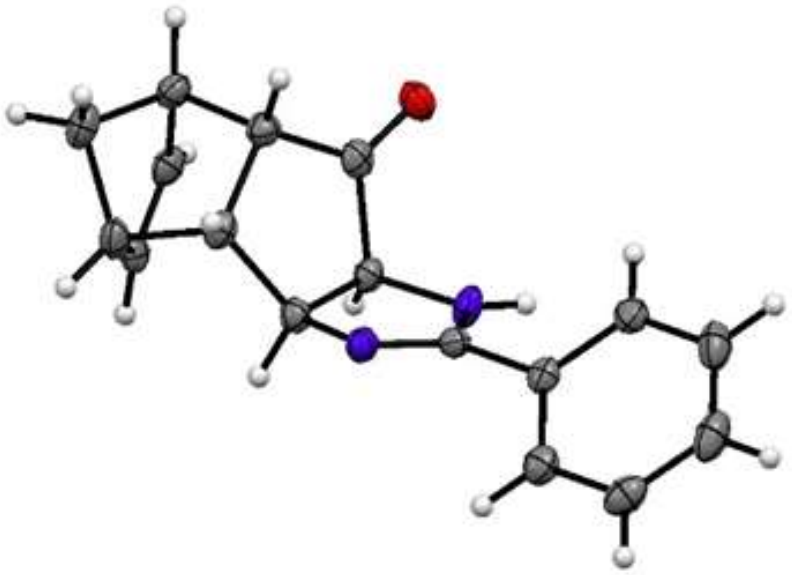


Figure S56. ^{1}H-^{1}H COSY NMR of compound **8d**

Table S1. Crystal data and structure refinement for CCDC 1974406 (3f)

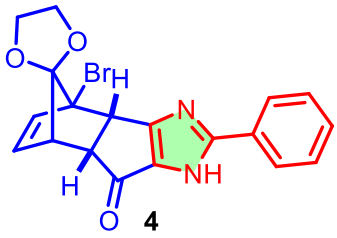


3f

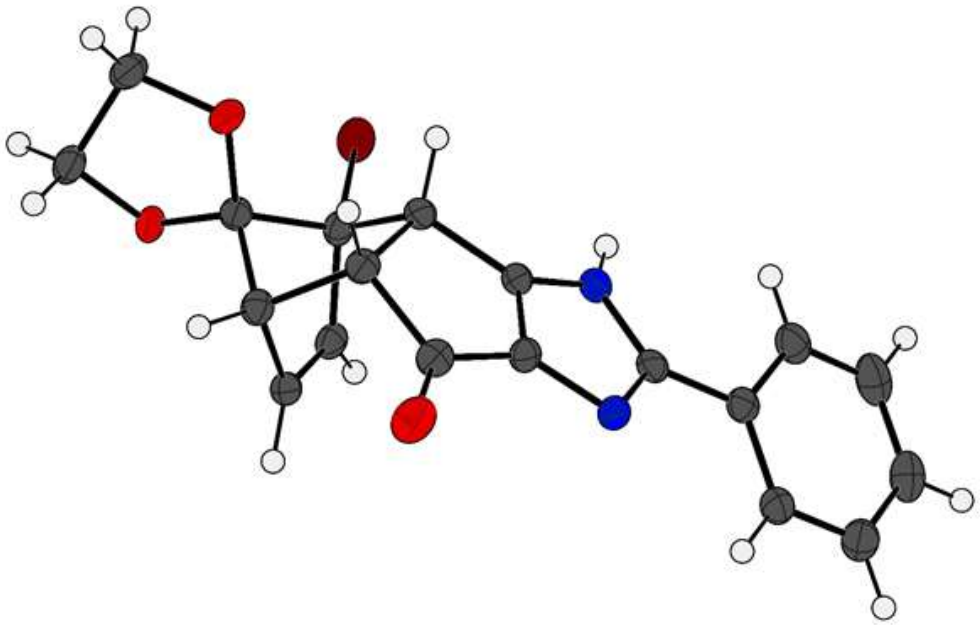


Identification code	INN-SOHAN-II-29
Empirical formula	$C_{17}H_{16}N_2O$
Formula weight	264.32
Temperature/K	150
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.5078(8)
b/Å	11.2634(9)
c/Å	12.0926(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1295.00(18)
Z	4
ρ_{calc}g/cm^3	1.356
μ/mm^{-1}	0.086
F(000)	560.0
Crystal size/mm^3	0.223 × 0.126 × 0.102
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.942 to 49.986
Index ranges	-8 ≤ h ≤ 11, -13 ≤ k ≤ 7, -14 ≤ l ≤ 14
Reflections collected	7151
Independent reflections	2283 [R_{int} = 0.0540, R_{sigma} = 0.0551]
Data/restraints/parameters	2283/0/181
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.0942
Final R indexes [all data]	R_1 = 0.0532, wR_2 = 0.1008
Largest diff. peak/hole / e Å^{-3}	0.21/-0.20

Table S2. Crystal data and structure refinement for CCDC 2530978 (4)

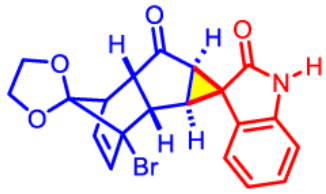


4

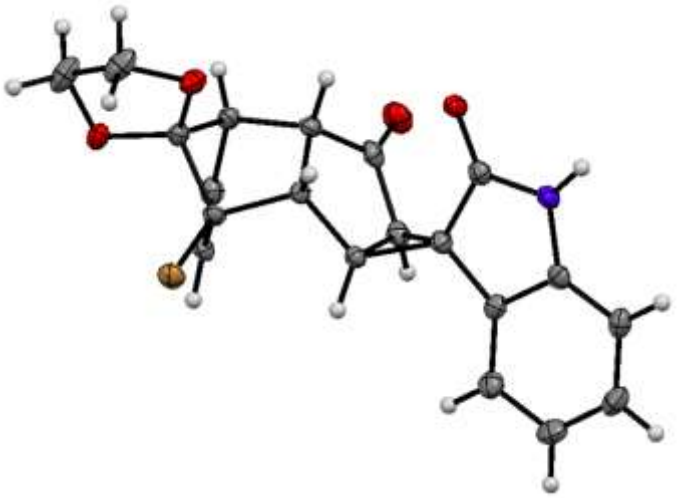


Identification code	INN_TGL_04_56_autored
Empirical formula	$C_{21}H_{21}BrN_2O_4S$
Formula weight	477.37
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.4144(4)
b/Å	9.5780(4)
c/Å	12.3679(5)
α/°	111.479(4)
β/°	95.220(3)
γ/°	101.940(3)
Volume/Å^3	998.15(8)
Z	2
ρ_{calc}g/cm^3	1.588
μ/mm^{-1}	2.195
F(000)	488.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.6 to 49.988
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -14 ≤ l ≤ 14
Reflections collected	35607
Independent reflections	3515 [R_{int} = 0.0999, R_{sigma} = 0.0375]
Data/restraints/parameters	3515/0/227
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.1003
Final R indexes [all data]	R_1 = 0.0403, wR_2 = 0.1031
Largest diff. peak/hole / e Å^{-3}	0.74/-0.77

Table S3. Crystal data and structure refinement for CCDC 1974453 (6a)

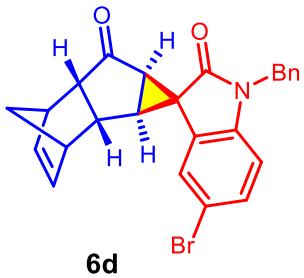


6a

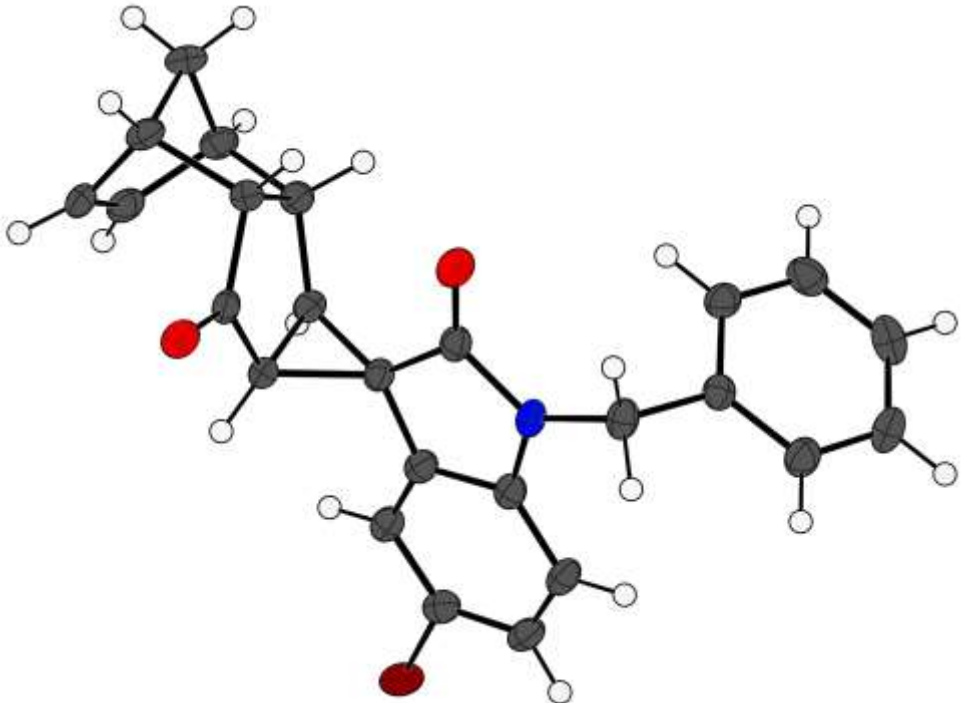


Identification code	INN-SOHAN-II-251-B
Empirical formula	$C_{20}H_{16}BrNO_4$
Formula weight	414.25
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	12.1893
B/ Å	6.7861
C/ Å	20.6372
α /°	90
β/°	93.489
γ /°	90
Volume/Å^3	1703.90
Z	4
ρ_{calc} g/cm^3	1.615
μ / mm^{-1}	2.439
F(000)	840.0
Crystal size/mm^3	0.207 × 0.12 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	5.024 to 49.99°
Index ranges	-14 ≤ h ≤ 14, -8 ≤ k ≤ 6, -23 ≤ l ≤ 24
Reflections collected	14616
Independent reflections	2997 [R_{int} = 0.0562,R_{sigma} = 0.0378]
Data/restraints/parameters	2997/0/235
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0328, wR_2 = 0.0717
Final R indexes [all data]	R_1 = 0.0400, wR_2 = 0.0756
Largest diff. peak/hole / e Å^{-3}	0.36/-0.41

Table S4. Crystal data and structure refinement for CCDC 1974434 (6d)

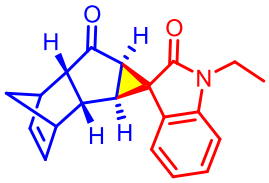


6d

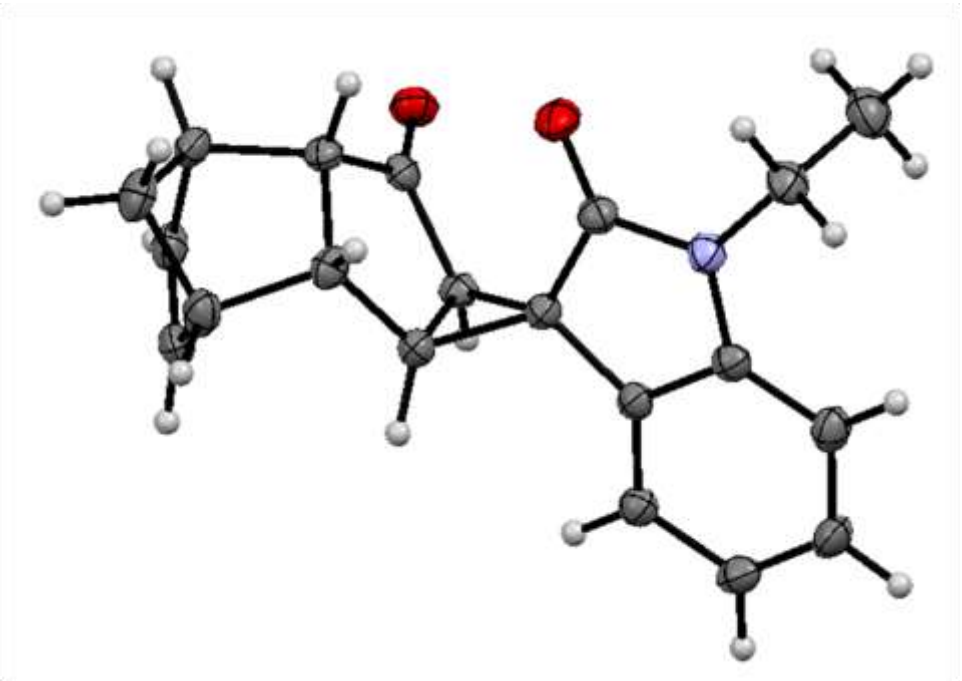


Identification code	INN-SOHAN-II-300
Empirical formula	$C_{25}H_{20}BrNO_2$
Formula weight	446.33
Temperature/K	150
Crystal system	triclinic
Space group	P-1
a/Å	8.7539(3)
b/Å	10.9118(4)
c/Å	12.2664(3)
α/°	66.662(3)
β/°	87.517(2)
γ/°	68.820(3)
Volume/Å^3	996.32(6)
Z	2
ρ_{calc}g/cm^3	1.488
μ/mm^{-1}	2.085
F(000)	456.0
Crystal size/mm^3	0.24 × 0.18 × 0.124
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.696 to 49.986
Index ranges	$-10 \le h \le 8$, $-12 \le k \le 12$, $-14 \le l \le 14$
Reflections collected	7281
Independent reflections	3478 [R_{int} = 0.0667, R_{sigma} = 0.0556]
Data/restraints/parameters	3478/0/262
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0385, wR_2 = 0.0978
Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.1013
Largest diff. peak/hole / e Å^{-3}	1.41/-0.41

Table S5. Crystal data and structure refinement for CCDC 1992116 (6e)

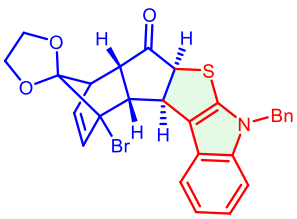


6e

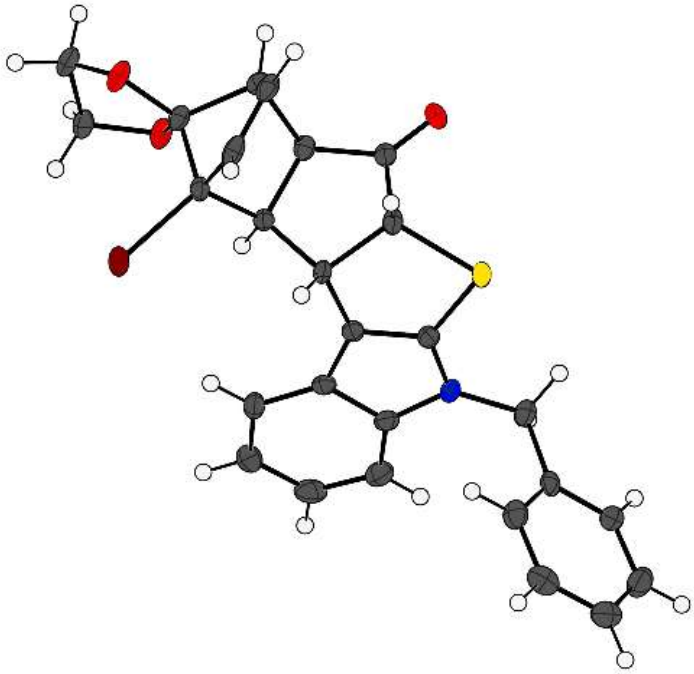


Identification code	INN-SOHAN-II-330_Mo
Empirical formula	$C_{20}H_{19}NO_2$
Formula weight	305.379
Temperature/K	150.00
Crystal system	triclinic
Space group	P-1
a/Å	8.3696(4)
b/Å	9.9170(4)
c/Å	20.0570(9)
α/°	96.597(3)
β/°	94.003(4)
γ/°	112.839(4)
Volume/Å^3	1512.14(12)
Z	4
ρ_{calc}g/cm^3	1.341
μ/mm^{-1}	0.086
F(000)	648.4
Crystal size/mm^3	0.24 × 0.18 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.66 to 50
Index ranges	-12 ≤ h ≤ 10, -14 ≤ k ≤ 14, -27 ≤ l ≤ 23
Reflections collected	15873
Independent reflections	5295 [R_{int} = 0.0469, R_{sigma} = 0.0690]
Data/restraints/parameters	5295/0/417
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0444, wR_2 = 0.0986
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.1064
Largest diff. peak/hole / e Å^{-3}	0.35/-0.39

Table S6. Crystal data and structure refinement for CCDC 1992303 (8c)



8c



Identification code	INN-SOHAN-II-350_Mo
Empirical formula	$C_{27}H_{22}BrNO_3S$
Formula weight	520.42
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.4378(5)
b/Å	10.0604(4)
c/Å	21.4824(10)
α/°	90
β/°	101.308(5)
γ/°	90
Volume/Å^3	2212.04(18)
Z	4
ρ_{calc}g/cm^3	1.563
μ/mm^{-1}	1.984
F(000)	1064.0
Crystal size/mm^3	0.123 × 0.113 × 0.078
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.976 to 49.996
Index ranges	-11 ≤ h ≤ 12, -11 ≤ k ≤ 11, -25 ≤ l ≤ 24
Reflections collected	11757
Independent reflections	3886 [R_{int} = 0.0414, R_{sigma} = 0.0477]
Data/restraints/parameters	3886/0/298
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0745
Final R indexes [all data]	R_1 = 0.0482, wR_2 = 0.0812
Largest diff. peak/hole / e Å^{-3}	0.36/-0.40

Table S7. Cartesian coordinates for the optimized geometries at B3LYP/6-31G(d) (solvent model, MeCN) level of theory (All energies are reported in Hartrees)

1
E = -3033.405557
G = -3033.276282

C	1.19125000	-0.83919900	-0.78604500
C	2.25217000	-1.26007200	0.30693800
C	2.22721500	0.99680000	0.46726500
C	1.17681100	0.71589400	-0.67270600
H	1.49114500	-1.20629600	-1.77397900
H	1.44641400	1.23272300	-1.59906700
C	1.97579700	-0.20798400	1.40783300
H	2.70097000	-0.25830200	2.22520400
H	0.96340400	-0.25037600	1.82389400
C	3.58677200	-0.74659900	-0.22649300
H	4.34714600	-1.36906000	-0.68819800
C	3.57068100	0.59331500	-0.13341200
H	4.31353700	1.29240400	-0.50538800
H	2.21111000	-2.31463800	0.58769300
H	2.15962400	2.00007400	0.89212300
C	-0.26110500	1.07931100	-0.31571200
C	-0.22714500	-1.24835000	-0.49585100
H	-0.54818200	-2.28566300	-0.49147900
C	-1.02088400	-0.19132400	-0.24941300
O	-0.69742400	2.20602700	-0.12461900
Br	-2.86671800	-0.22399500	0.13462100

5
E = -438.600176
G = -438.511992

C	2.52732100	-0.74926600	0.00004600
C	1.29202600	-1.42303500	0.00007300
C	0.12520800	-0.66424600	0.00000300
C	0.13780500	0.77380600	-0.00004300
C	1.39186800	1.41825900	-0.00003000
C	2.56856900	0.65626600	-0.00000400
H	3.45203600	-1.32165600	0.00008100
H	1.25132300	-2.51081400	0.00010600
H	1.44833200	2.50584200	-0.00000900
H	3.53196100	1.16308900	0.00000900
C	-1.22282200	1.21182900	0.00008100
H	-1.58010900	2.23494300	0.00026600
C	-2.06510400	0.07472100	-0.00019900
N	-1.20368000	-1.05178100	-0.00005700
H	-1.54522200	-2.00308300	0.00017000
O	-3.33272400	-0.06198300	0.00002700

Intermediate (1+5)
E = -3472.024599
G = -3471.782602

C	-1.06017400	1.26371600	-0.75578600
C	-1.07235200	2.35927800	0.37236100
C	-3.25571900	1.79223400	0.23215900
C	-2.56172800	0.83936200	-0.82517700
H	-0.71461700	1.71651500	-1.68895200
H	-3.03428500	0.94096700	-1.80759400
C	-2.16994600	1.83912900	1.33329900
H	-2.41126900	2.56039700	2.12070800
H	-1.93766700	0.87598600	1.79519400
C	-1.81639900	3.53823900	-0.24809500
H	-1.34124900	4.43040900	-0.64638600
C	-3.11386800	3.19772400	-0.34038200
H	-3.91289600	3.75075600	-0.82544600
H	-0.08909100	2.56967300	0.79613500
H	-4.26227400	1.47544500	0.51431700
C	-2.61044600	-0.62518500	-0.41900400
C	-0.22744300	-0.05802000	-0.52503900
C	-1.23802700	-1.04024300	0.08802200
O	-3.59775800	-1.33904100	-0.48961900
C	5.09935300	0.78340100	-0.83258600
C	4.67833600	0.49049100	0.47755600
C	3.32333400	0.26655800	0.70079100
C	2.34759000	0.32682000	-0.35094200

TS-(1+5)
E = -3471.990935
G = -3471.751295

C	1.79119800	-0.93961800	-0.98173800
C	2.19608500	-2.09567400	0.00765000
C	3.73452100	-0.50464800	0.47076200
C	2.88453500	0.14000700	-0.67627100
H	1.83946300	-1.30327400	-2.01484000
H	3.51524700	0.35192800	-1.54844600
C	2.63889800	-1.27690000	1.24665000
H	3.05082800	-1.90740900	2.04222500
H	1.85370300	-0.63357000	1.65538400
C	3.55021400	-2.60434800	-0.48102500
H	3.69643900	-3.52017000	-1.04696900
C	4.46732100	-1.66490400	-0.19557000
H	5.51498600	-1.65515000	-0.48364800
H	1.43836300	-2.86886400	0.14476300
H	4.34778400	0.20541100	1.03039500
C	2.11938200	1.42434100	-0.34947600
C	0.44818700	-0.20361100	-0.81437600
C	0.74622400	1.13958500	-0.55501400
O	2.67420400	2.50839500	-0.05480300
Br	-0.57863700	2.51671200	-0.54379900
C	-4.74866200	-1.25103000	-0.80265100
C	-4.35018000	-0.36264100	0.21162200
C	-3.03675200	-0.43718300	0.66357000
C	-2.10094200	-1.37296400	0.13732900
C	-2.52135100	-2.24388100	-0.87524800
C	-3.84690800	-2.18251100	-1.33605500
H	-5.77004500	-1.21237300	-1.17339500
H	-5.04974600	0.35739900	0.62967000
H	-1.82985300	-2.96922100	-1.29964200
H	-4.17537100	-2.86267000	-2.11846200
C	-0.81606200	-1.12425800	0.77104800
C	-1.05398900	-0.10789000	1.78937400
N	-2.39016400	0.29124800	1.65659700
H	-2.77201100	1.09279500	2.14082500
O	-0.27524200	0.39239400	2.62814300
H	-0.37403000	-0.48524400	-1.46301400
H	-0.10431200	-1.91079000	0.97174000

TS-XVIIa
E = -3471.994710
G = -3471.750818

C	-0.96224900	1.07499100	-0.94490800
C	-0.06813800	2.36257400	-1.02449000
C	-1.29944300	2.76624800	0.83405700
C	-1.76113500	1.34763300	0.38121100
H	-1.63469800	1.06000700	-1.80505600
H	-2.84474900	1.31223400	0.23138000
C	0.19632100	2.67386100	0.47687600
H	0.73592400	3.61509400	0.62536600
H	0.70534500	1.87374900	1.02234200
C	-1.04418300	3.49480000	-1.34676100
H	-1.17316900	3.93092000	-2.33326600
C	-1.78095600	3.72788200	-0.24826900
H	-2.63102700	4.39704400	-0.15160600
H	0.78597800	2.28175300	-1.69840200
H	-1.55876800	3.01481000	1.86536000
C	-1.41289400	0.17775300	1.29181000
C	-0.36755900	-0.38228700	-0.84876200
C	-0.95515500	-0.93353400	0.41313700
O	-1.54467700	0.12921300	2.51115700
Br	-3.27673500	-1.67226600	-0.11312700
C	5.11921700	0.24805200	0.41750400
C	4.61514000	-1.05753900	0.38193300
C	3.26842000	-1.23740900	0.08559600
C	2.35185200	-0.15979800	-0.15938500
C	2.91567200	1.13396400	-0.15434100
C	4.27124200	1.32715600	0.13571700
H	6.16839800	0.41795900	0.64456300
H	5.25859400	-1.91498400	0.56362900
H	2.32563200	2.00401800	-0.39251400

C	2.79957400	0.62621900	-1.65227700
C	4.16485100	0.84843200	-1.88082400
H	6.15372600	0.96102400	-1.03103100
H	5.39561800	0.43613800	1.29439600
H	2.09465800	0.68903400	-2.47977600
H	4.50637700	1.07796200	-2.88852700
C	1.06665500	0.04198900	0.22258200
C	1.25467300	-0.19429200	1.60877600
N	2.63849700	-0.04435600	1.86136700
H	3.04560100	-0.17224200	2.77769900
O	0.43911000	-0.49615600	2.54307600
H	-0.00979200	-0.42235800	-1.54015900
H	-1.19800900	-0.99285500	1.18156100
Br	-0.83242100	-2.93371100	-0.29319900

TS-XVIa
E = -3471.999704
G = -3471.756754

C	-0.83156100	0.86484000	-0.91735400
C	0.03949100	2.15936600	-0.74510700
C	-1.74106100	2.60616700	0.57526200
C	-2.05409800	1.17056600	0.01352500
H	-1.13997300	0.75863200	-1.96024100
H	-3.01441900	1.16282100	-0.51024700
C	-0.20605300	2.51629000	0.74347700
H	0.24228400	3.47572000	1.02248500
H	0.11006600	1.74338200	1.44783200
C	-0.76352800	3.27283800	-1.41373400
H	-0.55584100	3.68001600	-2.39942900
C	-1.82436200	3.53619200	-0.63119800
H	-2.65747400	4.19944700	-0.84601600
H	1.07553900	2.04730400	-1.07010100
H	-2.33665400	2.87963400	1.44907700
C	-2.10233000	0.05816200	1.05685800
C	-0.19685700	-0.51031200	-0.44846300
C	-1.10972100	-1.00103800	0.66159500
O	-2.79899000	0.03901500	2.06027600
Br	-2.93485500	-2.04603100	-0.78674900
C	5.35070700	-0.45377900	-0.64329700
C	4.78941900	-0.46613200	0.64322800
C	3.40271900	-0.49067000	0.75488400
C	2.53733600	-0.49699700	-0.39495700
C	3.13121400	-0.47660200	-1.67159500
C	4.52564800	-0.45706200	-1.78313700
H	6.43181500	-0.43664100	-0.75584300
H	5.42195200	-0.45869500	1.52831000
H	2.51140300	-0.47490300	-2.56588800
H	4.98104800	-0.44332000	-2.77115500
C	1.20043500	-0.51519800	0.11019700
C	1.26726100	-0.52601900	1.49356900
N	2.59609800	-0.49551000	1.89258600
H	2.91866000	-0.55244600	2.84872600
O	0.22289700	-0.54635200	2.26679200
H	-0.24974500	-1.21137500	-1.28575000
H	-1.07062200	-1.97490200	1.11730200

9
E = -3472.011501
G = -3471.764084

C	1.71853800	0.21210300	-1.03500300
C	2.16772000	-1.29417000	-1.15865500
C	3.87349900	-0.36807800	0.03151300
C	2.86843500	0.83671500	-0.15390100
H	1.66921500	0.66795200	-2.02568200
H	3.35549100	1.70539200	-0.60459000
C	2.85396800	-1.53350300	0.21911900
H	3.34321100	-2.50968600	0.27326100
H	2.17908800	-1.38487000	1.06591500
C	3.40455100	-1.24489200	-2.06796900
H	3.40460000	-1.51260400	-3.11675600
C	4.40744400	-0.69208300	-1.36610700
H	5.39096300	-0.41871900	-1.72603900
H	1.37138100	-1.97775700	-1.44703300
H	4.59530700	-0.19426800	0.82738300
C	2.35554800	1.15927000	1.23599600
C	0.38093200	0.47441200	-0.26057800
C	0.83969000	1.00937700	1.10249000
H	4.66813500	2.33945700	0.13319900
C	1.05426500	-0.76335400	-0.44682300
C	1.28174900	-2.21407000	-0.45670200
N	2.59257700	-2.43576800	-0.06289600
H	3.01613000	-3.35420600	-0.05986400
O	0.49315700	-3.13618300	-0.76348800
H	-0.65901400	-0.94446100	-1.74243400
H	-0.74585500	-1.91948000	0.79127800

6
E = -3472.030174
G = -3471.787116

C	0.93764300	0.91403200	1.28580500
C	0.24998900	2.27200300	1.67967800
C	0.86837600	2.60463300	-0.49409100
C	1.37468100	1.15042400	-0.19367000
H	1.81103900	0.74682100	1.92418200
H	2.45994200	1.06087300	-0.30766200
C	-0.44661300	2.66542400	0.34798300
H	-0.85482800	3.67921100	0.38460900
H	-1.20978600	1.95870100	0.04100200
C	1.40747000	3.29231500	1.66978200
H	1.88540700	3.68554100	2.55732100
C	1.76808900	3.49050700	0.39273400
H	2.60119600	4.07480600	0.02477900
H	-0.36339500	2.23604200	2.57872900
H	0.81006500	2.85871500	-1.55138100
C	0.80568600	-0.01916300	-1.00851800
C	0.18585800	-0.41872700	1.28999800
C	0.34825300	-1.11085000	-0.03863000
O	0.70405600	-0.05576900	-2.23701100
Br	3.84981900	-1.47956300	-0.55599900
C	-4.77691800	0.35427600	-1.29240900
C	-4.67820500	-0.59589200	-0.26821500
C	-3.41427700	-0.91762200	0.20906500
C	-2.24273100	-0.27998100	-0.27332000
C	-2.35587000	0.59422300	-1.35264000
C	-3.62760700	0.92353400	-1.84599000
H	-5.75379500	0.62240700	-1.67701600
H	-5.56118200	-1.08561300	0.12286300
H	-1.47551900	0.99198400	-1.83617000
H	-3.71292900	1.61581700	-2.67483300
C	-1.08344800	-0.88930400	0.44935800
C	-1.68649800	-2.04161200	1.25006500
N	-3.06123700	-1.91979800	1.12444800
H	-3.71723600	-2.54402000	1.58182200
O	-1.08062100	-2.87725100	1.93194100
H	0.26133100	-1.02336000	2.18571300
H	0.71394300	-2.11982200	-0.16647400

TS-(1+7)
E = -3794.950949

C	1.61461300	-1.18373600	-0.87791300
C	1.94103400	-2.23039200	0.25196700
C	3.68422500	-0.79797800	0.40910600
C	2.84253600	-0.21565000	-0.77569200
H	1.56786100	-1.69286100	-1.84687200
H	3.43742700	-0.20673500	-1.69763600
C	2.55789100	-1.31203000	1.33870900
H	2.93944400	-1.87382800	2.19817100
H	1.88780500	-0.51883700	1.68661700
C	3.19235600	-2.96841400	-0.21881500
H	3.19197600	-3.96506900	-0.65121600
C	4.23038700	-2.12188200	-0.11577300
H	5.25151500	-2.28517700	-0.44924700
H	1.11115100	-2.87991800	0.53653300
H	4.41112900	-0.10087800	0.83241800
C	2.25799400	1.19053500	-0.61345400
C	0.36824900	-0.26624300	-0.78152200
C	0.85783300	1.05973300	-0.71656300
O	2.96753500	2.22414300	-0.52488800
Br	-0.29166600	2.57262200	-0.94451700
C	-4.65789900	-1.61854600	-0.93348800
C	-4.39388500	-0.50312600	-0.12639800
C	-3.11095200	-0.38454200	0.40353200
C	-2.08674300	-1.32861100	0.14884500
C	-2.37011600	-2.42758600	-0.66845800

O	3.03664000	1.40119800	2.26504400
Br	-2.27056900	3.58252300	-0.67095600
C	-3.40018600	-3.69665900	-0.31629600
C	-3.07017000	-3.15181100	0.92637500
C	-2.11255600	-2.14200200	0.96729900
C	-1.45692000	-1.66601900	-0.22977600
C	-1.81309400	-2.23645100	-1.46287900
C	-2.77924200	-3.24075800	-1.49555100
H	-4.14658800	-4.48028500	-0.37211800
H	-3.55013900	-3.50233100	1.83211000
H	-1.34074400	-1.89501800	-2.37693400
H	-3.05914400	-3.68149800	-2.44582600
C	-0.52244000	-0.65864400	0.19696300
C	-0.67220300	-0.55054600	1.55628900
N	-1.60680900	-1.41811700	2.06131900
H	-1.87178500	-1.53152400	3.03212700
O	0.06401700	0.43474600	2.19790300
H	-0.19669200	1.24237500	-0.78939900
H	0.50705800	2.02626100	1.08825600

7
E = -761.575288
G = -761.488671

C	-2.94623100	-0.77448300	-0.00057800
C	-1.71243700	-1.43516500	-0.00053900
C	-0.55364600	-0.65411000	-0.00023200
C	-0.59201600	0.77625200	-0.00005000
C	-1.85031700	1.41161700	-0.00009400
C	-3.01107100	0.63469600	-0.00038200
H	-3.86483600	-1.35616800	-0.00072100
H	-1.65834900	-2.52151000	-0.00056000
H	-1.91734800	2.49785800	-0.00008700
H	-3.98300500	1.12328100	-0.00052900
C	0.76909600	1.22779600	-0.00033400
H	1.11146300	2.25494500	-0.00078300
C	1.60146400	0.11075400	0.00035900
N	0.77878400	-1.01744800	0.00025400
H	1.13639100	-1.96273600	0.00089000
S	3.34344700	-0.04360500	0.00069400

Intermediate-(1+7)
E = -3794.997132
G = -3794.756340

C	-0.99212300	1.33790900	-0.74257600
C	-1.02718300	2.35886000	0.45501500
C	-3.22050400	1.91445800	0.13674600
C	-2.50139700	0.97923000	-0.91632800
H	-0.58071100	1.83896000	-1.62243500
H	-2.90585400	1.13545100	-1.92180800
C	-2.21186200	1.84179700	1.30751500
H	-2.46976100	2.52743100	2.12098400
H	-2.05884300	0.84220400	1.72397100
C	-1.67010000	3.60831000	-0.14107500
H	-1.12636900	4.49589000	-0.45227100
C	-2.97190000	3.33924900	-0.34243000
H	-3.70719000	3.95904200	-0.84714200
H	-0.06660800	2.49543000	0.95434500
H	-4.25786700	1.63506100	0.33342400
C	-2.62978000	-0.49716600	-0.57143000
C	-0.23038600	-0.03079900	-0.57441500
C	-1.28987500	-1.01123900	-0.06062900
O	-3.65173600	-1.15434200	-0.67925400
C	5.02779000	0.84000600	-1.09268300
C	4.69839400	0.48732900	0.22066500
C	3.35515000	0.23176500	0.50910100
C	2.32749600	0.32187400	-0.47639500
C	2.69011700	0.67907000	-1.79060200
C	4.03168300	0.93303200	-2.08654000
H	6.06459600	1.04471900	-1.34826500
H	5.46302900	0.41230900	0.99057900
H	1.93745000	0.76189800	-2.57196300
H	4.31362300	1.20870200	-3.10030600
C	1.07867200	-0.00582100	0.16458000
C	1.36235600	-0.28965200	1.50605000
N	2.73924700	-0.13453800	1.68579600
H	3.19531500	-0.29396600	2.57344800
H	-0.00785200	-0.33797900	-1.60583500
C	-3.66049300	-2.57024400	-1.19903400
H	-5.65026400	-1.74516300	-1.35849300
H	-5.16332300	0.23598900	0.08034700
H	-1.60371200	-3.16744200	-0.88776000
H	-3.89108000	-3.42775500	-1.82614600
C	-0.85880700	-0.82957700	0.78056400
C	-1.27071500	0.32206300	1.56588300
N	-2.57675900	0.59360500	1.24220800
H	-3.08796900	1.37809400	1.62617500
H	-0.44198600	-0.49208300	-1.46937800
H	-0.15444000	-1.50604900	1.24082700
S	-0.38282800	1.21093400	2.70740300

8
E = -3795.018440
G = -3794.777815

C	-1.28883200	0.76614200	0.51886600
C	-1.05436900	0.02665400	1.88811500
C	-3.25360900	-0.34222200	1.51929200
C	-2.80069300	0.48877300	0.25260500
H	-1.08110000	1.83162600	0.63598300
H	-3.41615200	1.38804500	0.13968800
C	-1.98727700	-1.20100200	1.74852300
H	-2.04477100	-1.79520000	2.66613900
H	-1.73776400	-1.85867600	0.90821200
C	-1.83772000	0.83338700	2.91802700
H	-1.39591900	1.53843600	3.61638200
C	-3.14592600	0.61798800	2.69638800
H	-3.98949200	1.10811900	3.17351900
H	-0.00534800	-0.16116100	2.11893400
H	-4.20742000	-0.85677700	1.38616900
C	-2.89073900	-0.30613700	-1.03757200
C	-0.48416100	0.26039700	-0.73786500
C	-1.51397500	-0.43448900	-1.68714900
O	-3.91787600	-0.76542100	-1.51208000
Br	1.22239600	3.48964200	-0.87808300
C	4.33924400	-1.60296600	1.27063500
C	3.60789500	-2.53316500	0.52979500
C	2.38780700	-2.11535900	-0.00934800
C	1.88584800	-0.78678100	0.16758800
C	2.65469200	0.13120400	0.90932200
C	3.86626300	-0.28576700	1.45697600
H	5.29022200	-1.89836900	1.70645200
H	3.97159000	-3.54684500	0.38201400
H	2.30492600	1.15109600	1.04339700
H	4.46319200	0.41658500	2.03379900
C	0.61682300	-0.73485300	-0.50573900
C	0.41907900	-1.97625900	-1.05332800
N	1.46158200	-2.82454000	-0.76725700
H	1.56216300	-3.77991700	-1.08066000
H	-0.09009900	1.15376900	-1.23158500
S	-1.05403900	-2.23733700	-1.98078200
H	-1.55342100	0.03104500	-2.67639700

TS-XVIIIb
E = -3794.979966
G = -3794.738552

C	-0.80201000	0.89036500	-0.95062700
C	0.01096100	2.21539600	-0.73420600
C	-1.87645400	2.61456200	0.44479000
C	-2.10764000	1.16958000	-0.13496200
H	-1.01726800	0.75606500	-2.01341900
H	-3.01344600	1.15069900	-0.74901600
C	-0.35600600	2.57778700	0.72613800
H	0.03623800	3.55568500	1.02564300
H	-0.06422100	1.82355700	1.46067900
C	-0.77629400	3.29408700	-1.47545500
H	-0.50980300	3.69714000	-2.44861500
C	-1.89889300	3.53186500	-0.77535400
H	-2.73502200	4.16465100	-1.05941500
H	1.07127500	2.13676200	-0.98129700
H	-2.54467900	2.87533000	1.26862700
C	-2.25089500	0.03847900	0.88006600
C	-0.17887300	-0.46412900	-0.40838000
C	-1.21551200	-1.00236100	0.56257000
O	-3.09218700	-0.02360100	1.76621200

H	-1.28752900	-1.06717400	1.03512000
Br	-0.95624600	-2.87401600	-0.61948800
S	0.37769100	-0.75751200	2.87664400

10
E = -3794.985075
G = -3794.747430

C	0.99788400	0.53477700	1.24032500
C	0.57015200	1.81918500	2.02819900
C	1.06787700	2.61609500	-0.03745100
C	1.38945500	1.08307200	-0.15766800
H	1.86232500	0.07613100	1.73321300
H	2.45671900	0.93483200	-0.35995400
C	-0.14590500	2.63281100	0.93004000
H	-0.39572800	3.64795900	1.25496800
H	-1.04421500	2.14993300	0.55552500
C	1.85384800	2.64634800	2.14952600
H	2.45731400	2.72635700	3.04900300
C	2.14541700	3.12410700	0.92795400
H	3.03851400	3.66250500	0.62444600
H	0.02428200	1.62939400	2.95542600
H	0.97548200	3.14996400	-0.98597800
C	0.72129500	0.16491800	-1.17978900
C	0.07212000	-0.66238200	0.98618800
C	0.11553600	-1.03415800	-0.45935700
O	0.74612400	0.30072400	-2.39220900
Br	4.18274200	-1.15638400	-0.69185000
C	-4.75576600	1.33763200	-1.12262500
C	-4.78770700	0.15464800	-0.37683800
C	-3.56606300	-0.41892500	-0.03878600
C	-2.32009000	0.14923200	-0.36349600
C	-2.31726900	1.29227500	-1.16698000
C	-3.53415100	1.88530700	-1.53185800
H	-5.68815500	1.81519000	-1.41017300
H	-5.72646200	-0.31453600	-0.09697500
H	-1.39569300	1.72946900	-1.53120700
H	-3.52255700	2.77968400	-2.14815700
C	-1.26261600	-0.78588800	0.15192900
C	-2.04199600	-1.99898600	0.62666900
N	-3.34677800	-1.65873200	0.57543700
H	-4.08382200	-2.29923700	0.84733800
H	0.11019300	-1.44752900	1.73385100
S	-1.47102700	-3.48579200	1.14477600
H	0.31861000	-2.02906500	-0.84925400

TS-XIXb
E = -3794.953795
G = -3794.712777

C	-0.97221600	1.13676400	-1.00635600
C	-0.13684900	2.45925600	-1.16130300
C	-1.42755800	2.92952300	0.64098400
C	-1.78648400	1.45188400	0.30055600
H	-1.63807800	1.04549700	-1.86637400
H	-2.86343500	1.32249700	0.16504300
C	0.07628900	2.90219800	0.31591000
H	0.55848900	3.88199300	0.39656200
H	0.61551600	2.18224000	0.93780800
C	-1.16855200	3.50691100	-1.58487800
H	-1.30021300	3.85995800	-2.60359400
C	-1.94369500	3.77308300	-0.52077600
H	-2.83303300	4.39569400	-0.49004800
H	0.73526900	2.37638500	-1.81200000
H	-1.72122600	3.24191000	1.64529400
C	-1.33677000	0.38697500	1.29699700
C	-0.33732400	-0.29431300	-0.82888700
C	-0.81536600	-0.75915700	0.49771300
O	-1.42221400	0.43631500	2.51910600
Br	-3.34298000	-1.57157900	0.16511400
C	5.05406400	0.60847700	0.61028000
C	4.62946700	-0.72031500	0.56557600
C	3.30612000	-0.96894800	0.20643500
C	2.34729400	0.04860100	-0.07857100
C	2.83623200	1.37162800	-0.07496500
C	4.16307400	1.63841100	0.27170300
H	6.08040500	0.84039800	0.88139400
H	5.30923700	-1.54095900	0.77883500
H	2.21614000	2.20288300	-0.36464600
Br	-2.74238800	-2.09547200	-1.03944000
C	5.23147100	-0.36606300	-1.04437200
C	4.83754700	-0.38484400	0.29729800
C	3.46896900	-0.41714900	0.57380900
C	2.47945100	-0.41747700	-0.45891900
C	2.90726000	-0.39469700	-1.80066700
C	4.27458600	-0.37146000	-2.08073400
H	6.29026300	-0.34381000	-1.28984800
H	5.57308900	-0.37885200	1.09829900
H	2.18179800	-0.39174600	-2.61134300
H	4.60950600	-0.35506100	-3.11529900
C	1.20066800	-0.43375600	0.19397400
C	1.43023500	-0.45496600	1.55809200
N	2.79820600	-0.43838500	1.78555800
H	3.22821500	-0.46992700	2.69946100
H	-0.12725400	-1.15359900	-1.25634000
S	0.19035200	-0.51662500	2.77649500
H	-1.16212000	-1.95318800	1.06139200

H	4.50845200	2.66895100	0.26669100
C	1.09502400	-0.63833600	-0.41932900
C	1.41676500	-2.06141500	-0.42438900
N	2.70568700	-2.19816900	0.00903200
H	3.17511300	-3.09320800	0.05682400
H	-0.62775100	-0.93485400	-1.66627700
S	0.49331400	-3.40192600	-0.92910100
H	-0.66281800	-1.74399200	0.90483100